UNIVERSITY OF ILLINOIS

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

RICHARD E. DRURY

ENTITLED THE EFFECTS OF ALUMINUM OXIDE ON REACTIONS OF

FREE CHLORINE WITH 2,4-DICHLOROPHENOL

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF BACHELOR OF SCIENCE IN THE CHEMISTRY CURRICULUM

Instructor in Charge

APPROVED:

HEAD OF DEPARTMENT OF CHEMISTRY

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THE EFFECTS OF ALUMINUM OXIDE ON REACTIONS OF FREE CHLORINE WITH 2,4-DICHLOROPHENOL

BY

RICHARD E. DRURY

THESIS

for the

DEGREE OF BACHELOR OF SCIENCE

in the

CHEMISTRY CURRICULUM

College of Liberal Arts and Sciences

University of Illinois

Urbana, Illinois

1967

To my parents,

Toshie Horiguchi and William Walter,

for their constant support in all of my endeavors.

ABSTRACT

THE EFFECTS OF ALUMINUM OXIDE
ON REACTIONS OF FREE CHLORINE
WITH 2,4-DICHLOROPHENOL

Richard E. Drury
University of Illinois at Urbana-Champaign, 1987

2,4-dichlorophenol was reacted with free chlorine in an aqueous, room temperature batch reaction, producing a mixture of the starting product and 2,4,6-trichlorophenol. The same reaction conducted in the presence of aluminum oxide resulted in many additional products, including such toxicologically significant compounds as polychlorodibenzofurans, and hydroxylated polychlorinated biphenyls. The alumina is observed promoting di- and trimerizations, ether formations, dechlorinations, oxidations, substitutions and epoxide openings.

The use of alumina in water treatment may be of health concern if reactions similar to those observed occur in drinking water.

A brief study of the fire which occured at the Javits Lecture Center, at the State University of New York at Stony Brook, may reveal how similar reactions of free chlorine with phenol occur on alumina surfaces at high temperatures in the gas phase.

ACKNOWLEDGEMENT

I gratefully acknowledge Dr. Richard Larson, my advisor, and Dr. Vernon Snoeyink for providing the original concept for this project. Sincere thanks go also to Dr. John Katzenellenbogen for his advice, guidance and sponsorship.

Special thanks are extended to Marianne Tozzo, who labored over many of the drawings in this work, and stayed up late nights helping me to complete the typing. But most of all I appreciate her continuous support, advice, encouragement, prodding, friendship and love.

I would also like to thank Don Maffetore, et al, for help in the final stages of this work.

Thanks go to all of those who provided technical advice regarding the Javits Lecture Center fire. These include: Drs. Paul Connett of St. Lawrence University; Arnold Schecter of SUNY at Binghamton Clinical Campus; Ted Goldfarb, Dale Deutsche, and David Parkinsson of SUNY at Stony Brook; expert panelists Phil Landrigan of Mount Sinai School of Medicine, Ellen Silbergeld of the Environmental Defense Fund, and Jim Mellus of the New York State Department of Health. Special thanks are due Dr. Stephen Levin of Mount Sinai School of Medicine, who was right from the beginning and was willing to do something about it.

I must also acknowledge all those who provided the political and organizational support necessary to bring the Lecture Center fire situation towards a more acceptable resolution, because good science is most effective when used together with good organizing and politics. Thanks to: Chris Vestuto, Sandra Hinson, John Kasionowicz and Bonnie Hain of the Stony Brook Graduate Student Organization; Marc Gunning and Gerry Shape of the Stony Brook Student Polity Association; Drs. Leland Marsh and William Wiesner of the United University Professions; Sheryl Carlin and Joanne Curtis of the Civil Service Employees Association; and Walter Hang and Steven "Rombo" Romalewski of the New York Public Interest Research Group.

There is no way to adequately thank two people without whom the Lecture Center problem would never have come to a resolution. Deepest thanks to Dave DeLucia, for having the tenacity of a pit bull, and to Regina Stephens Good for caring.

Finally, very special thanks to Nancy Wolff who knows me too well.

TABLE OF CONTENTS

I. INTRODUCTION

I.A. Statement of the Problem

Activated aluminum (Al_2O_3), also known as alumina, is finding progressively wider use in water treatment. Most of the available literature focuses on alumina's adsorptive capabilities for removal of fluoride, arsenic, and phosphate (Rubel, 1984; Rosenblum and Clifford, 1984; Bernhardt, et al, 1981; Hohl and Stumm, 1976) and organic matter (Davis and Gloor, 1981; Kummert and Stumm, 1980; Thomas, Bottero, and Leprince, 1983; Leprince, Bottero, Thomas, and Chen, 1984). Foerster and Solbach (1979) report development of a trial lignin removal process for the purification of pulpmill effluents, utilizing alumina. Point of use systems are currently employing alumina for the removal of inorganics such as Ar, Cr, F^-, and U (Lake, 1983). There has been recent research indicating the effectiveness of alumina in removing natural organic matter folowing preoxidation of water with ozone (Chen, Snoeyink, and Flessinger, unpublished).

In certain of these applications, the alumina may come in contact with significant concentrations of chlorine disinfectants, such as HOCl, OCl^-, NH_2Cl, etc. Chlorine which reaches the alumina surface may react with the alumina and the compounds adsorbed on it. The catalytic activity of alumina has been well documented, and often results in unexpected reaction products (see literature review).

Voudrias, Larson, and Snoeyink (1985) report recently that free chlorine reacts with phenol (a component of lignin in natural waters) adsorbed on granular activated carbon (GAC), promoting such reactions as hydroxylation of the aromatic ring, oxidation to quinones, chlorine substitution, carboxylation, and oxidative coupling (dimer formation). Most notable of products formed are chlorohydroxybiphenyls (hydroxylated PCB's) because of their potential toxicity.

Because of activated aluminum's catalytic capacity, including promotion of oxidation reactions, it is of interest to determine if free chlorine and phenols will react to form potentially toxic compounds in the presence of alumina.

I.B. Javits Lecture Center Fire

On September 26, 1986, a fire broke out in a storage room of the Javits Lecture Center on the State University of New York Stony Brook campus. The fire appears to have involved reactions of free chlorine with phenol on aluminum oxide surface. Combustion products included the extremely toxic polychlorinated dibenzofurans and polychlorinated dibenzo-p-dioxins.

While the fire in no way provided a controlled experiment, the analysis of the reactants, products, reaction conditions, and possible mechanisms may give us further insight into how the chemistry of free chlorine and phenol on aluminum oxide surface can have environmental significance. The study of the fire will be dealt with briefly in Section VI.

II. OBJECTIVES

1) Determine the aqueous room temperature reaction products of free chlorine and 2-4-dichlorophenol in the presence of aluminum oxide.

2) Study existing literature on aluminum oxide catalysis to determine its catalytic potential.

3) Propose mechanisms involved during the alumina catalyzed reactions of free chlorine and 2,4-dichlorophenol.

4) Conduct a brief case study of the Javits Lecture Center fire, including analysis of probable reactants, combustion products, reaction conditions, and mechanisms.

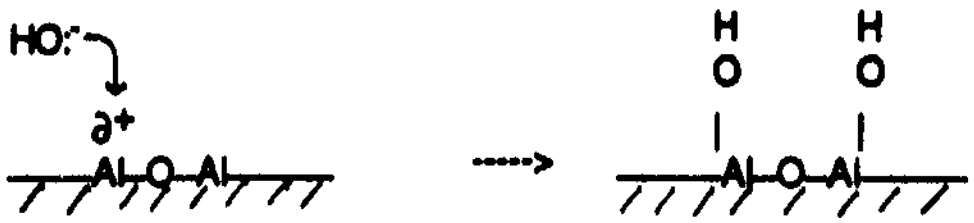
III. LITERATURE REVIEW

III.A Aluminum Oxide as a Catalyst

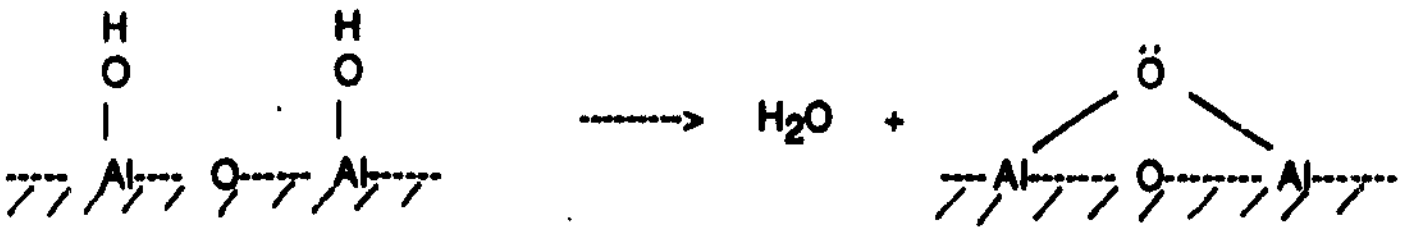
III.A.1. Physical Aspects of Alumina as a Catalyst (Linsen, 1970)

The most noted physical property of gamma-alumina is its extraordinary porosity, which is central to alumina's role as an adsorbant. However, alumina also displays extraordinary catalytic properties (see below). Alumina's peculiarly amphoteric nature is central to its role as a catalyst.

Exposed aluminum atoms on the alumina surface are electron deficient, and therefore, behave as Lewis acids. Thus, alumina surfaces adsorb water either as H_2O or as hydroxide ions, which form surface hydroxyl groups. The adsorbed hydroxyl groups behave as proton donors -- Brønstead acids.



When two neighboring hydroxyl groups combine to give water, they leave a strained oxygen bridge which behaves as a basic site.

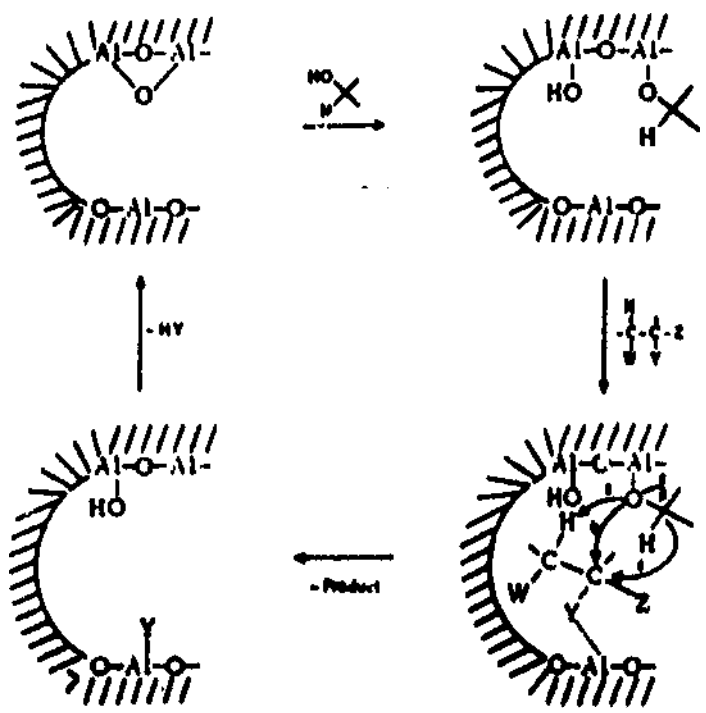


The loss of water can also leave an exposed aluminum atom, a Lewis acid.

Thus, a single gamma-alumina surface can act simultaneously as an acid and a base, with certain regions of the alumina surface populated with acidic hydroxyl groups, and aluminum atoms and other regions with alkaline oxygen bridges.

Posner remarks that the importance of steric factors in alumina catalysis has been noted (1978). The entropy of activation is lowered when a reactant and reagent are adsorbed closely on the alumina surface in an orientation suitable for chemical reaction. Posner further comments on the importance of the alumina in activating the

reactant or reagent. Posner offers the following scheme which explains possible reaction pathways on alumina and highlights the role of the alumina surface (1978).



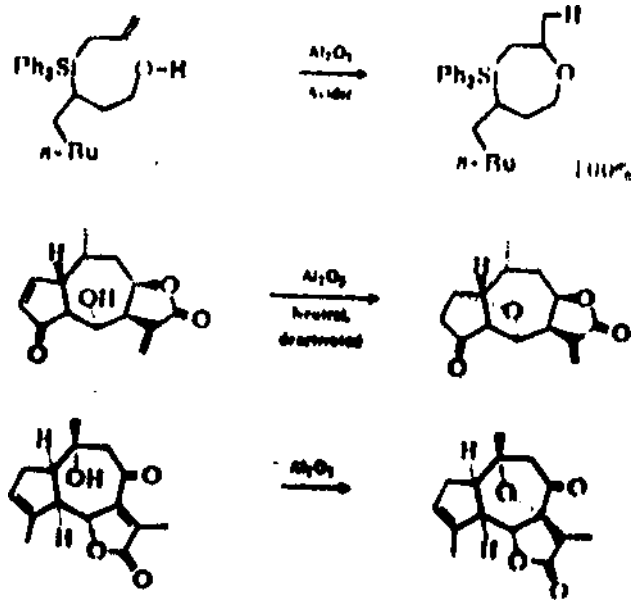
Scheme I. Possible pathways of reactions on alumina.

Possibilities	Pathway	Type of reaction
Case I	a	rarely observed
W, Y = O; Z = H	b	addition
(epoxides)	c	not observed
Case II	a	enolization
W = H; Y, Z = O	b	rarely observed
(aldehydes and ketones)	c	reduction-oxidation
Case III	a	elimination
Y = OH, OR, OTs,	b	substitution
or halogen	c	not observed

III.A.2. Addition Reactions[1]

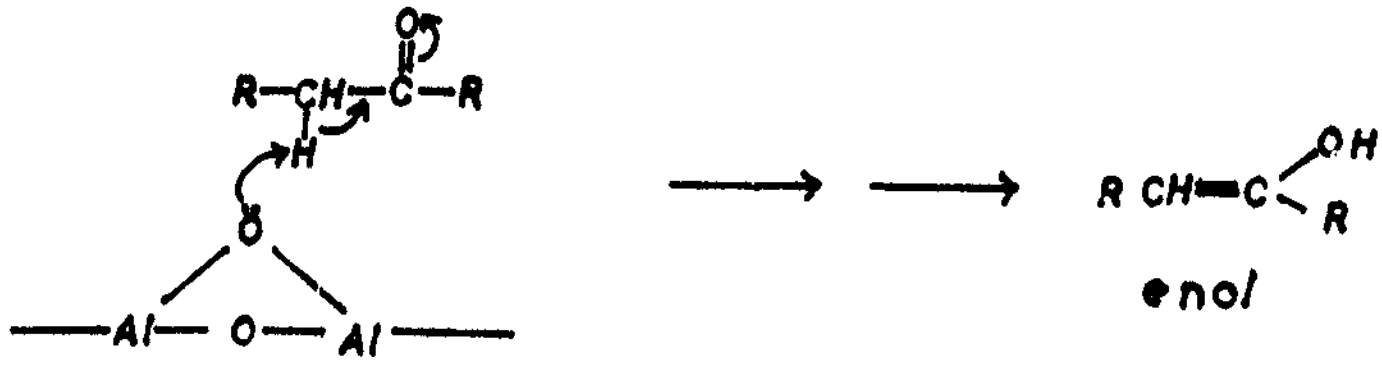
III.A.2.a. Intramolecular Addition of O-H Groups[2]

Posner (1978) cites several examples of intramolecular addition of OH to double bonds, both carbonyl-conjugated and non-conjugated. He emphasizes the importance of the intramolecularity of the reactions, because there have been no comparable intermolecular additions of alcohols to double bonds observed (Corriu et al, 1977; MacPhail et al, 1973; Irwin and Geleeman, 1969).

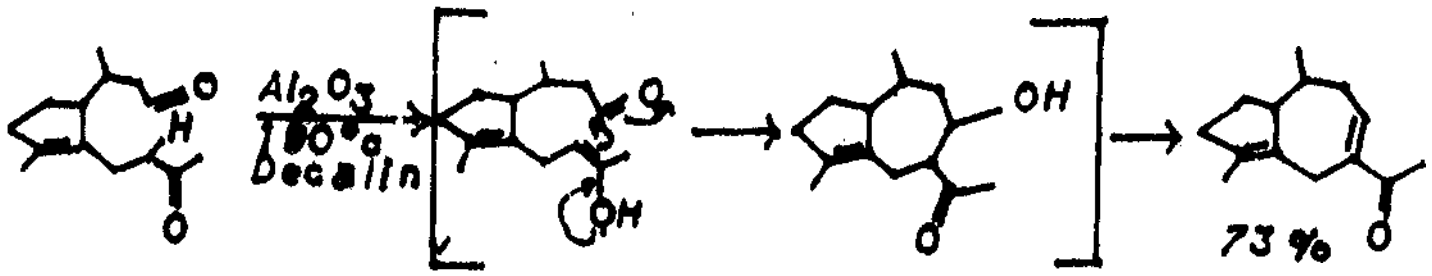


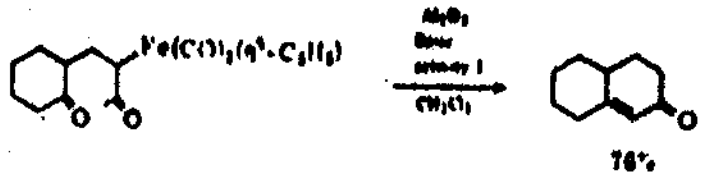
III.A.2.b. Intramolecular Addition of Acidic CH Groups

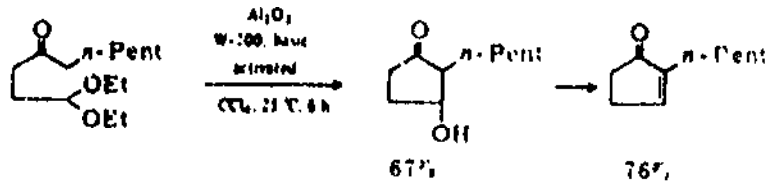
Alumina, acting as a base, can cause the enolization of ketones (Posner, 1978).



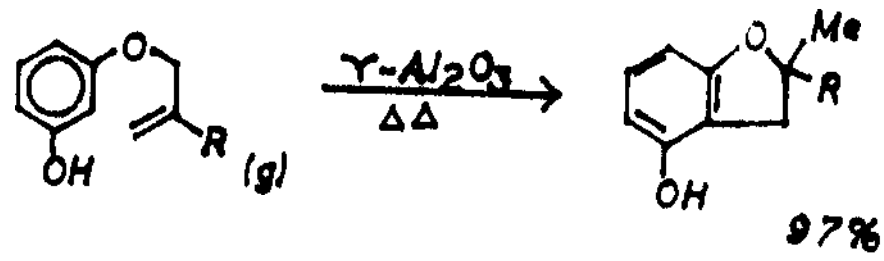
If there are carbonyl groups present in th · same molecule, the enolate ion can attack the non-enolized carbonyl group, resulting in carbocyclization. The reaction amounts to an intramolecular aldol condensation (Hoffman and Siegel, 1976; Rosan and Rosenblum, 1975; Posner and Lentz, unpublished).







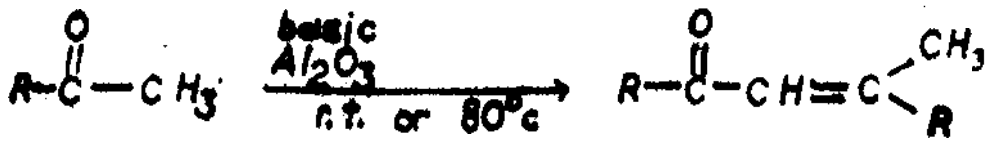
A seemingly similar cyclization is noted in a Japanese patent (Ube Industries, JP 60,100,566). This reaction differs from the above in that it involves a skeletal rearrangement, and although no mechanism is proposed, it does not appear to be an aldol condensation.

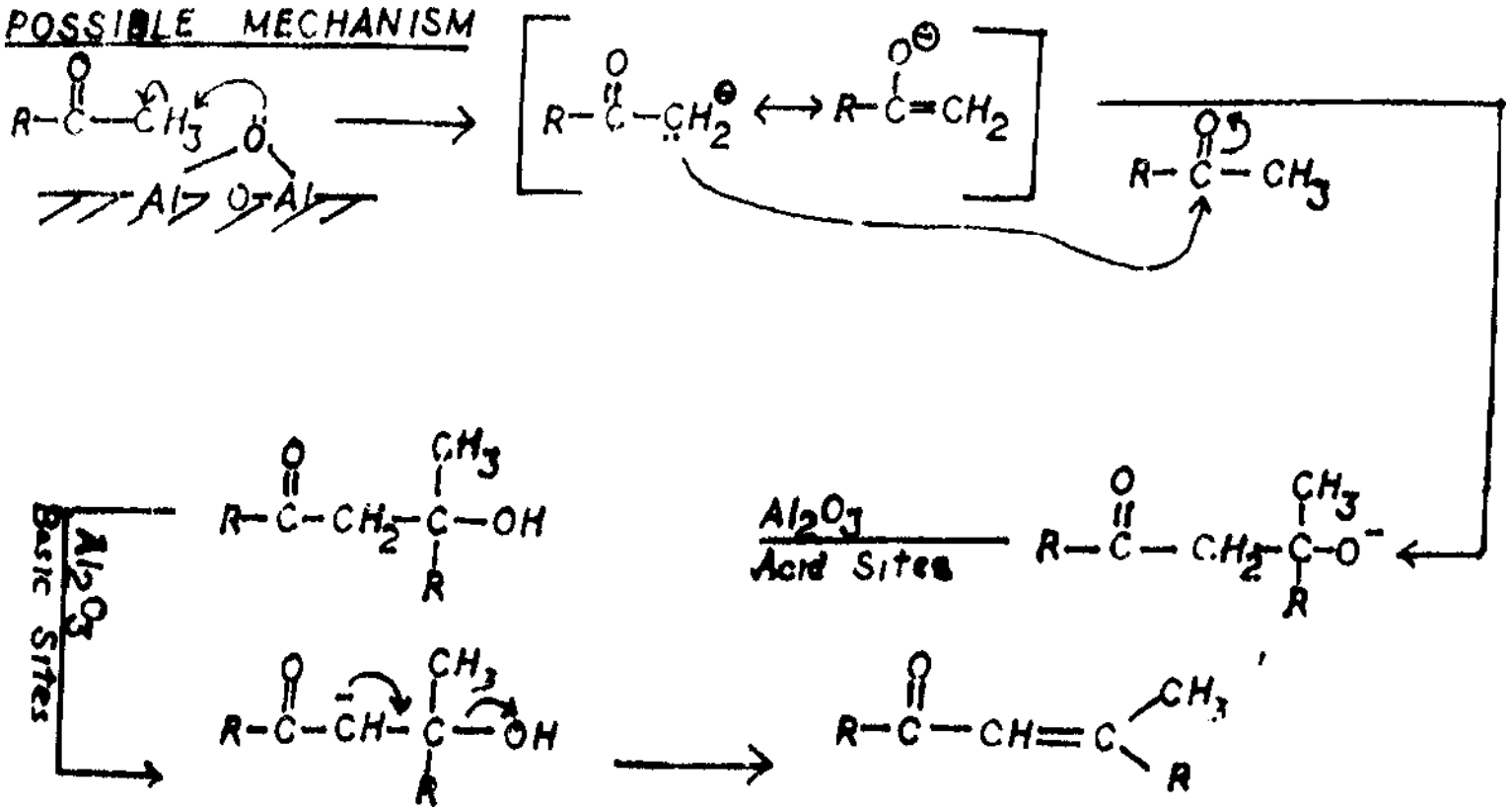


III.A.3. Intermolecular Condensation Reactions

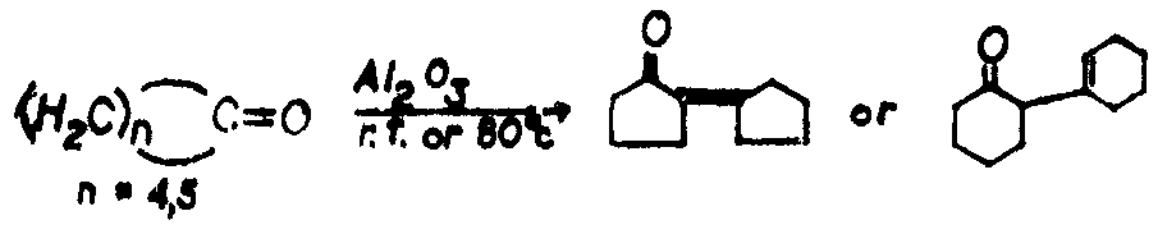
III.A.3.a. Aldol Condensations

Since Posner's Angewandte Chemie (1978 International Edition in English) article, there has been a great deal of research in the area of intermolecular condensation reactions catalyzed by gamma-aluminum oxide. These have proven to be some of the most interesting of the alumina-catalyzed reactions because of the relatively mild reaction conditions allowed. Alumina-catalyzed condensation reactions provide mild pathways to such products as chalcones and enones. Most examples in the literature are of basic gamma-alumina catalyzing aldol condensation reactions (Muzart, 1982).

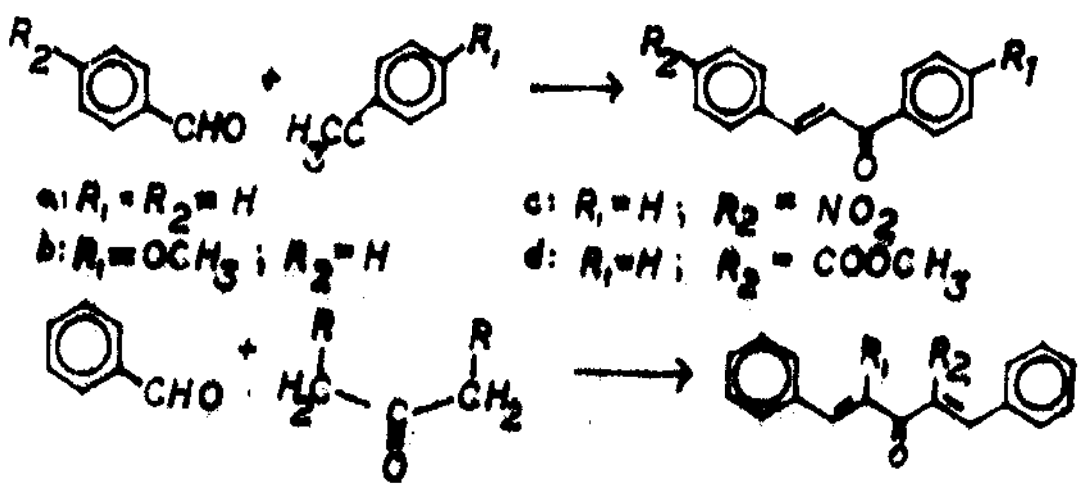




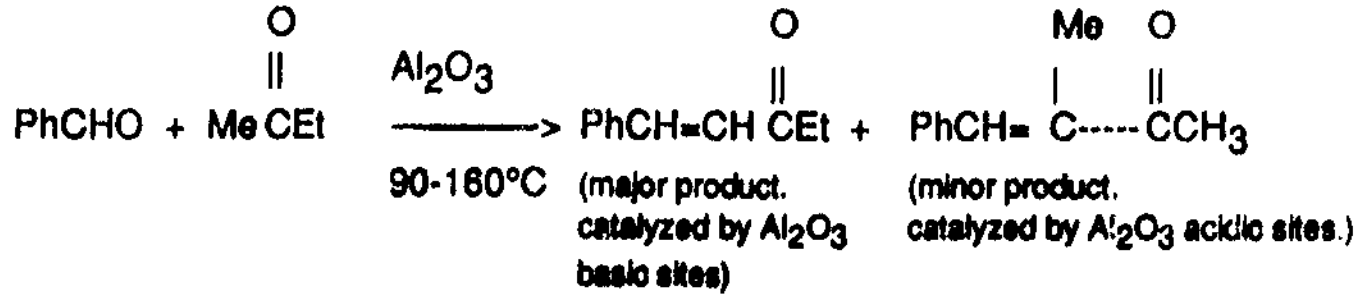
Muzart cites the following aldol condensation reactions, most likely with similar reaction mechanisms (1982):



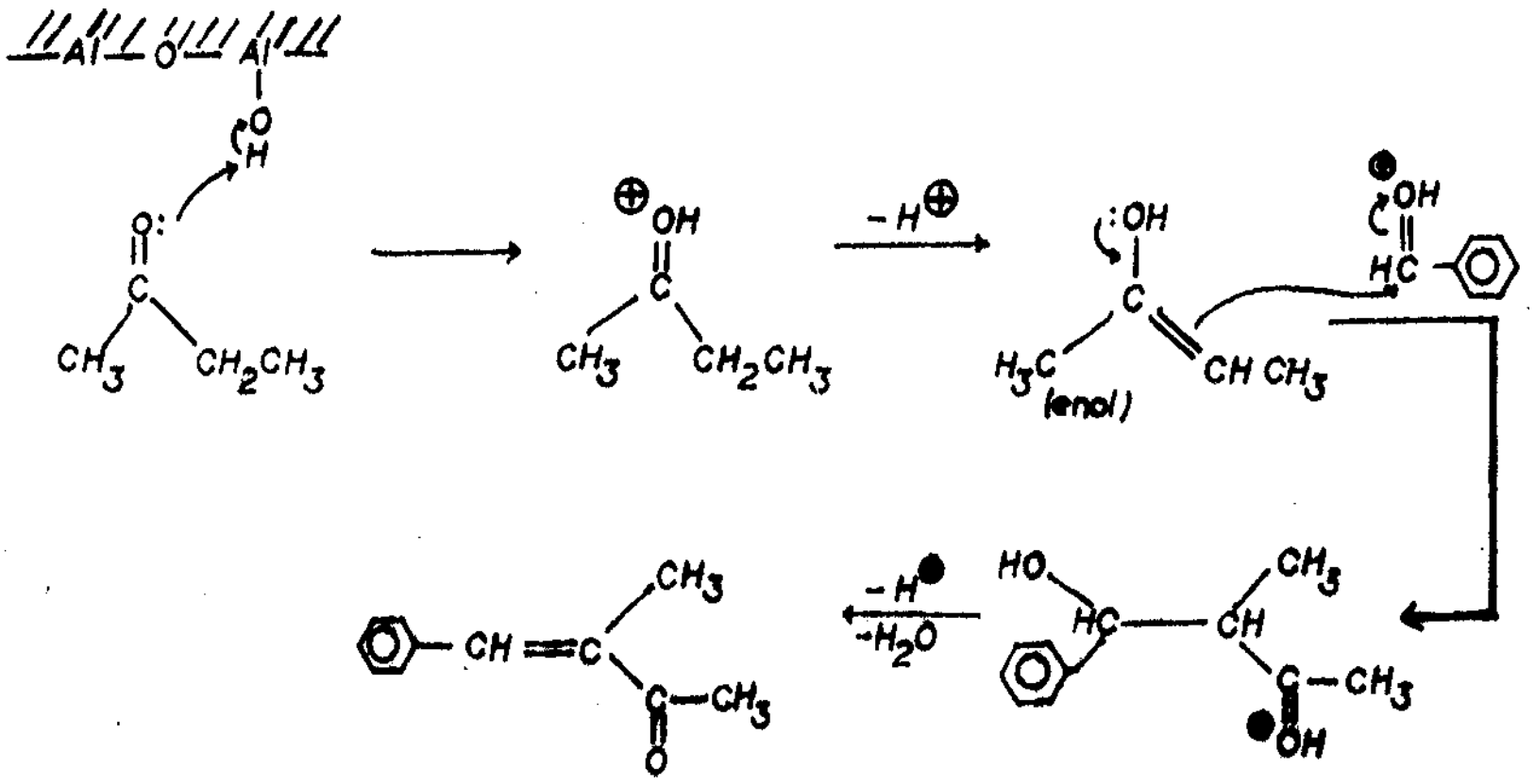
Varma et al note the following related reactions which provide a mild route to chalcones (1985):



Nondek and Malek describe an aldol condensation which displays gamma-alumina's amphoterism -- the alumina acting as both an acidic and alkaline catalyst (1980).



The base catalyzed reaction above requires abstraction of a proton from an alpha-carbon at the alumina surface (see section III.A.2.b.). Steric considerations favor removal of the proton from the methyl group of the methyl-ethyl ketone. This results in the base-catalyzed product by a mechanism almost identical to that in section III.A.2.b. The reactions catalyzed by the acidic sites on the alumina surface are initiated by addition of a proton to the carbonyl oxygen. The molecule them forms an enol thrcugh loss of a proton from an alpha-carbon. The proton is lost in this reaction from the alpha-carbon of the ethyl group of the methyl-ethyl ketone, since this produces the most stable enol. The result is the acid-catalyzed product by the following mechanism:



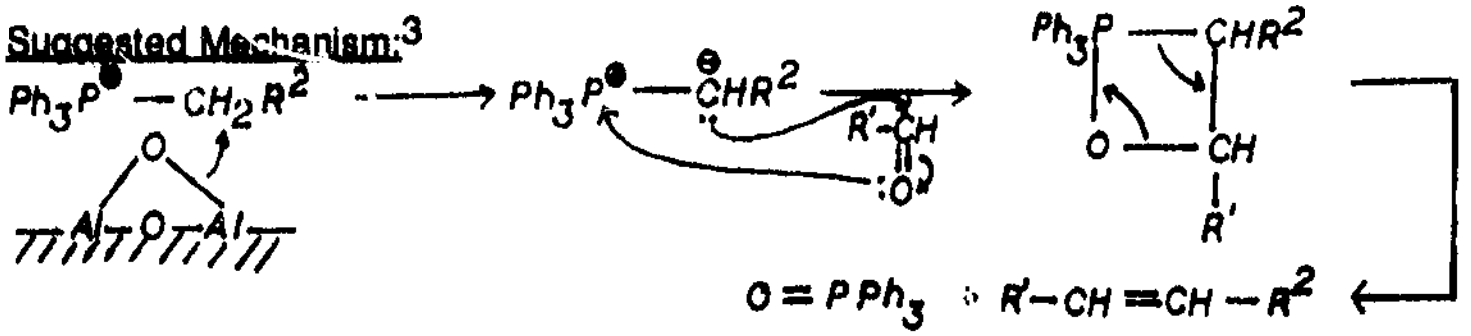
III.A.3.b. Wittig, Wittig-Horner, and Knoevenagel Condensations

Recent research reveals an interesting array of condensations akin to the aldol, all of which are catalyzed by basic sites on the alumina surface. Texier-Boullet notes the occurance of Wittig, Wittig-Horner, and Knoevenagel reactions in which the alumina surface is the catalyst, rather than the commonly used bases (Texier-Boullet et al, 1985).

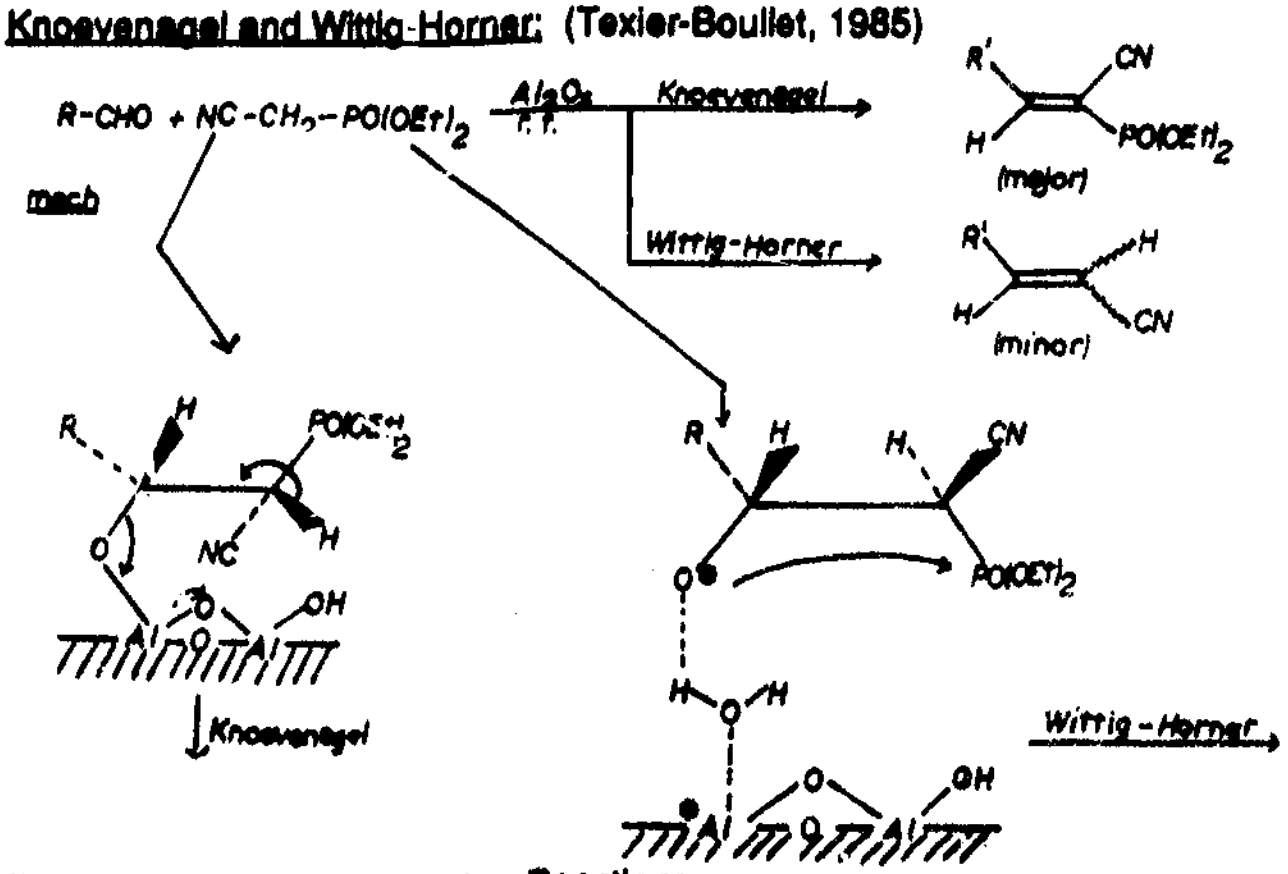
Wittig

$R'\text{-}CHO + Ph_3P^{+}\text{-}CH_2R^2, Cl^- \dashrightarrow R'\text{-}CH{=}CH\text{-}R^2 + O{=}PPh_3 + HCl$

Suggested Mechanism:[3]



Knoevenagel and Wittig-Horner: (Texier-Boullet, 1985)

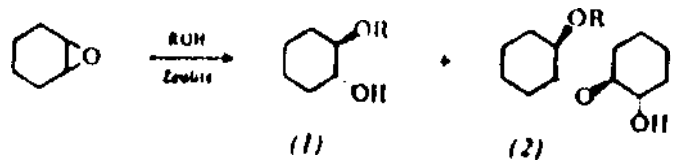


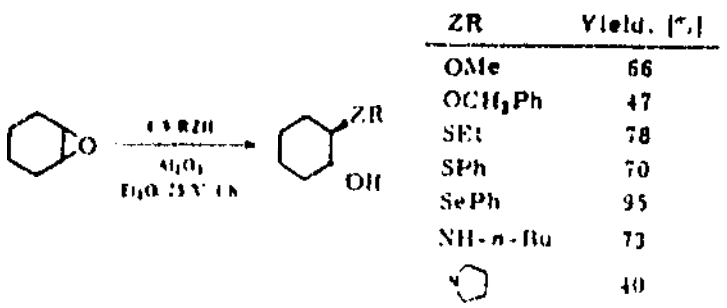
III.A.4. Intermolecular Addition Reactions

III.A.4.a. Intermolecular Addition of OH and Other Heteroatom-H Groups:

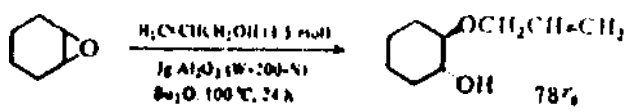
In 1974 Gary Posner et al began the study of the addition of heteroatom-H (RZ-H) species to electrophiles, using chromatographic alumina as catalyst. This work

focused on epoxides as the electrophiles, being opened by such nucleophiles as: alcohols, thiols, benzene selenol, amines, and acetic acid. The following are indicative of their findings: (Posner and Rogers, 1977; Posner and Romero, unpublished)



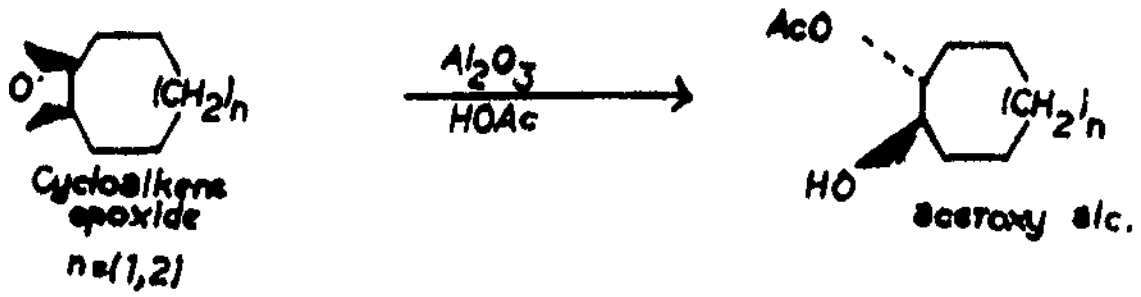


ZR	Yield, [%]
OMe	66
OCH_2Ph	47
SEt	78
SPh	70
SePh	95
NH-*n*-Bu	73
	40



30g (0.3 mol)

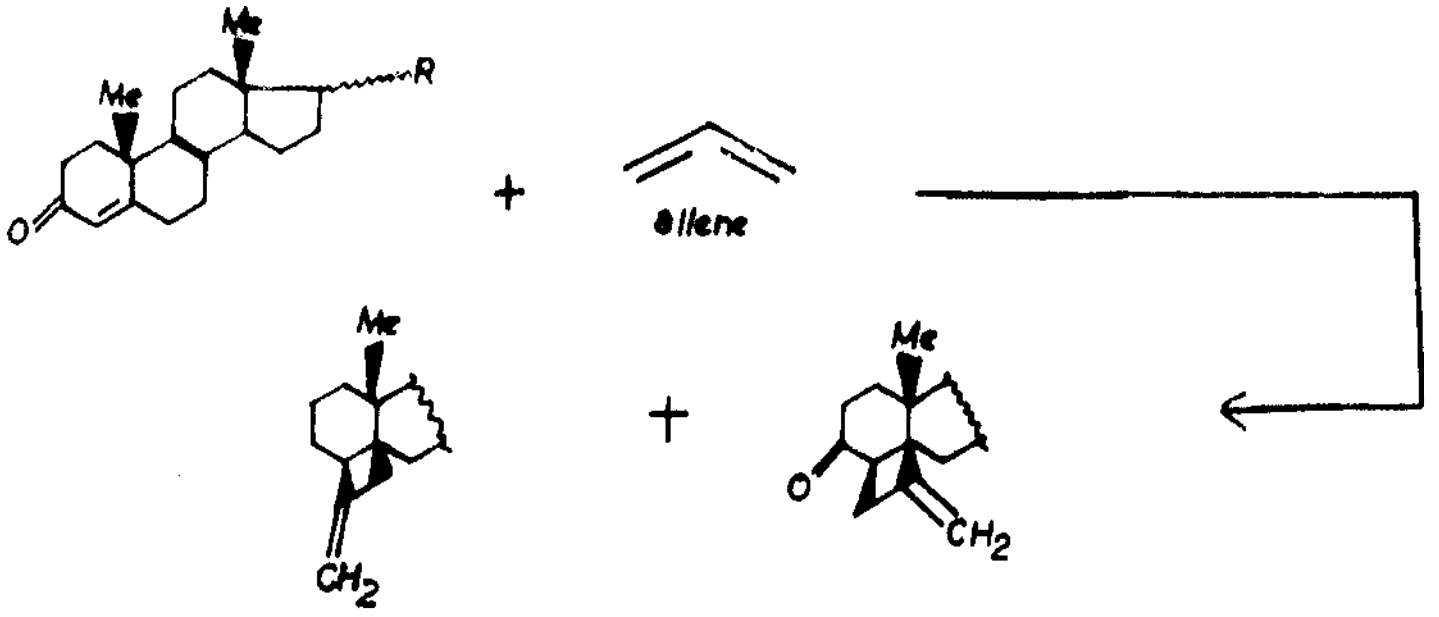
In 1981 Posner, Hulce and Rose published the following related reaction:



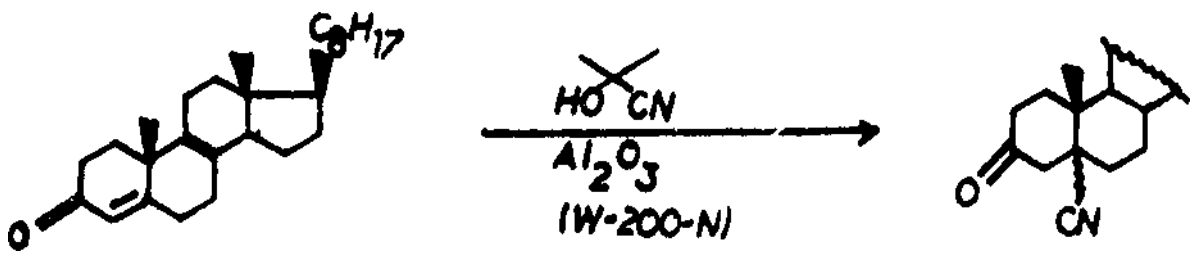
III.A.4.b. Intermolecular Addition of Acidic C-H Groups

The literature shows few examples of intermolecular additions of acidic C-H groups, but one of note is in a 1985 article by Farwaha et al. This article studies the addition of allene to a steroidal enone which is a polyaromatic conjugated carbonyl compound. He takes advantage of the peculiar steric features of the steroid to study the mechanism of the reaction. The steroid first was adsorbed to the alumina surface -- the less hindered alpha-face toward the surface, with hydrogen-bonding from the lone

pair of the ketone, and π-bonding from the bulk of the molecule. The more hindered beta-side is then open to attack from alkenes and allenes, through a 1-4 radical mechanism.



Posner and Mukharji (unpublished) cite the following example:



III.A.5. Reduction-Oxidation Reactions

Activated alpha-alumina has proven to be a highly specific promoter of room temperature oxidations and reductions of many types. M. J. Chapdelaine (Ph.D. dissertation, 1979) has studied alpha-alumina's role in carbonyl reductions and alcohol oxidations. He found that adsorption of 2-propanol to dried alumina facilitated very specific carbonyl reductions, such as allowing "alpha-beta unsaturated aldehydes to be reduced in a 1,2-fashion while permitting the survival of alpha-beta-unsaturated enones and other functional groups." Trichloroacetaldehyde adsorbed on activated alumina was found to be a mild oxidizing reagent.

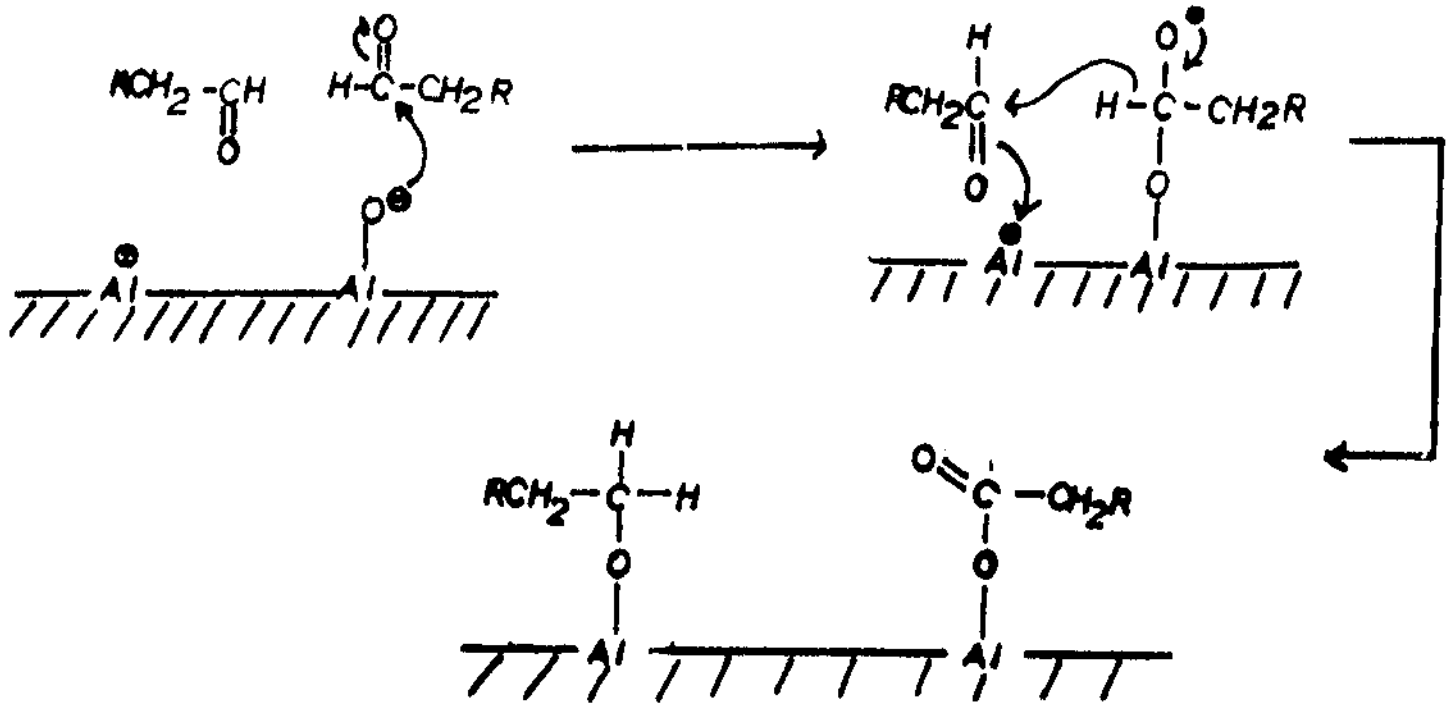
One of the better researched alumina-promoted oxidation-reduction reactions is one similar to the Canizzarro, in which the alumina surface acts as both an acid and a base. In 1974, F.A. Lamb et al discovered an alumina-catalyzed Canizzaro type

reaction for 9-(p-methoxyphenyl)- 9-fluorenylacetaldehyde, even though the normal base-catalyzed Canizzaro reaction would not proceed:

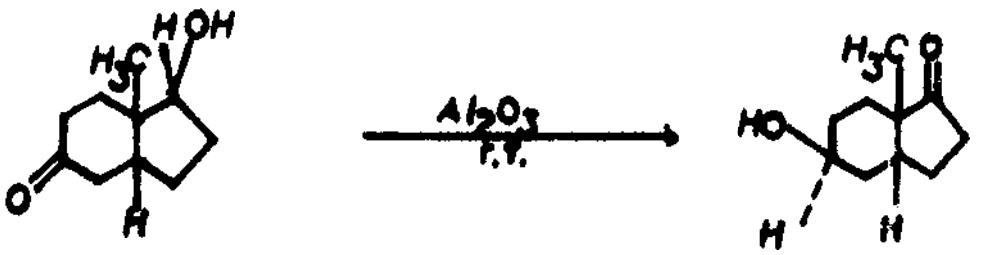
$$RCH_2COH \xrightarrow{Al_2O_3} RCH_2CH_2OH + (RCH_2COO)_3Al$$

R = [9-(p-methoxyphenyl) -9- fluorenyl]

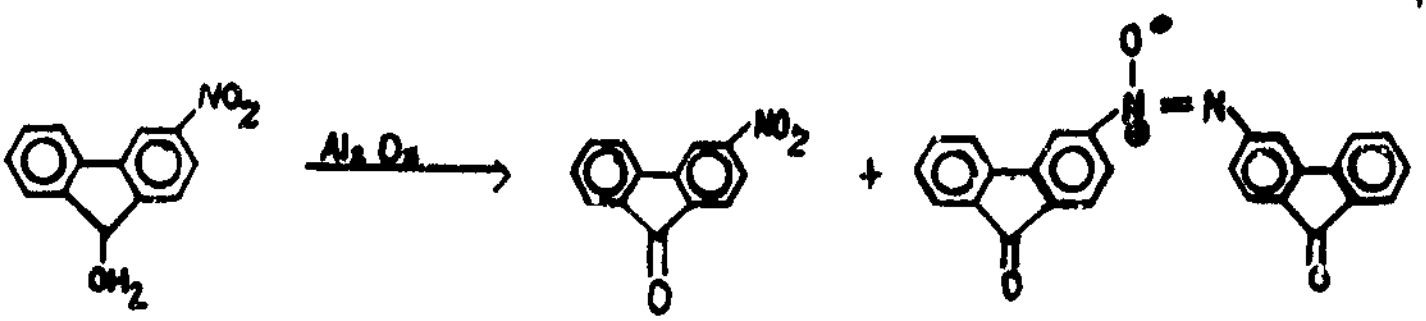
The mechanism proposed involves both acidic and alkaline sites on the alumina surface:



As early as 1959, room temperature alumina-catalyzed oxidation-reduction reactions were known. Acklin and Prelog (1959) cite the following internal redox reaction resulting in isomeric ketol:



H.L. Pan et al (1975) have reported that column chromatography over alumina of 3-nitrofluoren-9-ol results in two different oxidations to yield 46-48% 3-nitrofluoren-9-one and 25-30% 3,3'-azoxyfluoren-9-one.



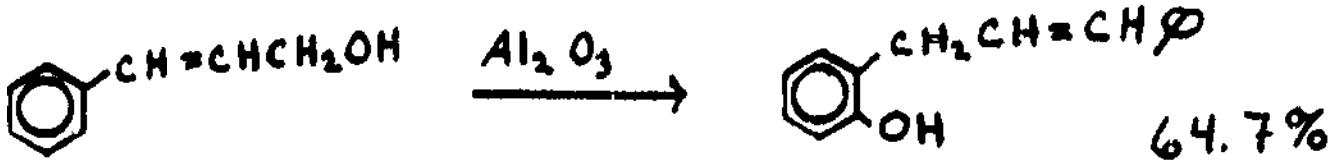
Kamogawa et al (1980) repcrt the following reduction-oxidation reaction during the alumina catalyzed dehydration of 4-(alpha-hydroxyethyl)phenols:

4-(alpha-hydroxyethyl)phenols

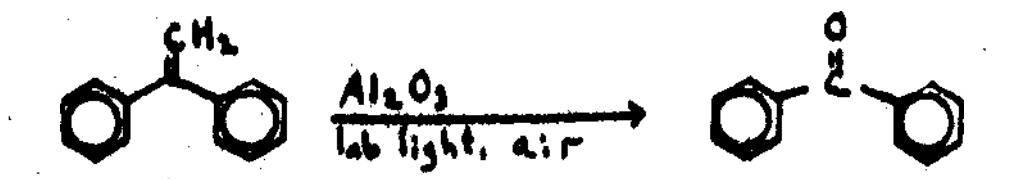
4-ethyl phenols

4-acetyl phenols
+ tautor ·rs

The following patent, filed in 1977 by Starks, Lundeen and Allan of Continental Oil (U.S. 4,105,698) company can be explained as an oxidation of the cinnamyl alcohol function to cinnamaldehyde and then a mixed aldol condensation with the phenol:

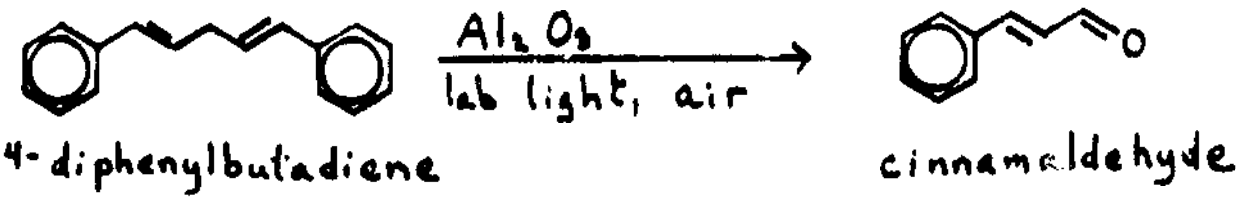


Aronovitch and Mazur (1985) note the following oxidative clevages of olefins in the presence of light and air on alumina support. They suggest that sometimes the reactions involve radical intermediates.

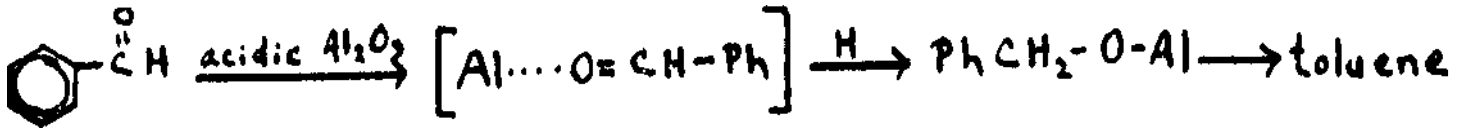


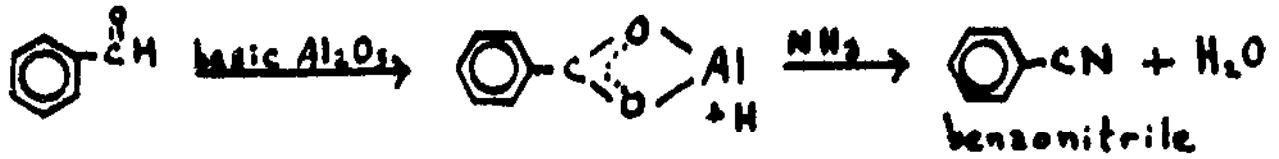
1,1-diphenyl ethylene

benzophenone



Niwa, Inagaki, and Murakami (1985) cite a benzaldehyde reduction catalyzed by acidic sites on the alumina surface, which occurs simultaneously with a benzaldehyde substitutio n reaction catalyzed at the basic sites:





Posner (1978) stresses the selectivity of alpha-alumina as an oxidation-reduction catalyst. He writes, "2-propanol on activated Woelm alumina is a reducing 'reagent' with selectivity comparable to, or in some cases even greater than that of the most sophisticated complex boron and aluminum hydride reducing agents. For example, chromone suffered reduction of both the aldehyde group and the alpha, beta double bond with the following reagents: $NaBH_4$, $NaBH_4/AlCl_3$, diisobutylaluminum hydride in tetrahydrofuran, and $NaB(CN)H_3$ in the presence of acid. However, 2-propanol on activated alumina selectively reduced the aldehyde group to give the allylic alcohol in 80% crude yield."

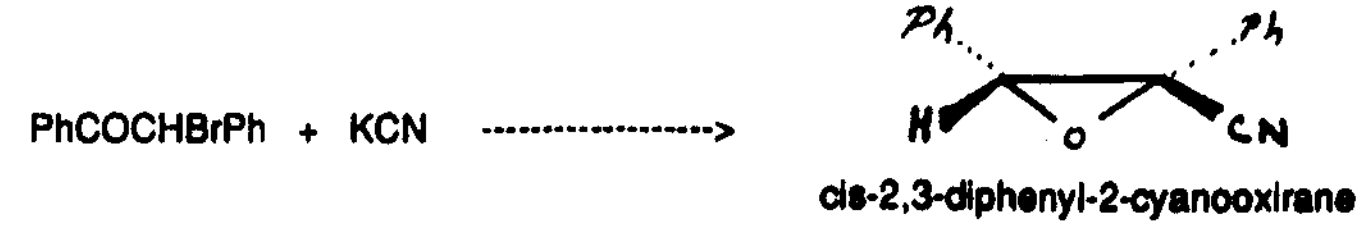
Clearly, alpha-Al_2O_3 is a very interesting and unique catalyst for oxidation-

reduction reactions, sometimes catalyzing reactions that would not occur under standard reaction conditions.

III.A.6. Substitution Reactions:

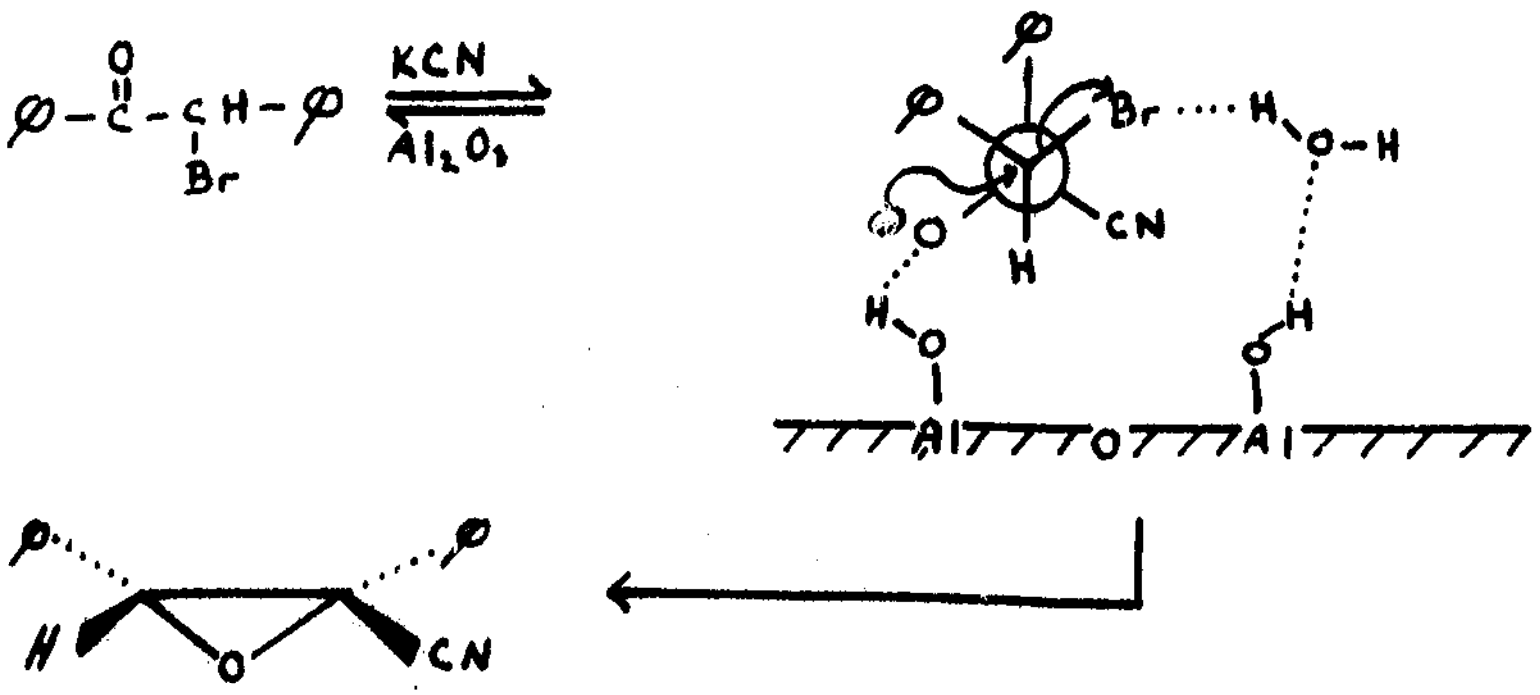
III.A.6.a. Intramolecular Substitution Reactions by Heteroatom Nucleophiles:

Takahashi, Nishizuka, and Iida (1981) reported the intramolecular substitution of bromine by carbonyl oxygen of increased nucleophilicity due to reaction of the carbonyl carbon with cyanide. The proposed mechanism utilizes Brønsted acid sites on the alpha-alumina surface, resulting in the trans, rather than the expected cis-isomer.



cis-2,3-diphenyl-2-cyanooxirane

mechanism:



Herwig, Huchler, et al reported in a BASF patent (U.S. 4,196130) a simple route to cyclic ethers from straight chain diols, utilizing dehydration over an alumina catalyst:

$-H_2O$, Alumina

$HO(CH_2)_4OH$ ----------> THF

$HO(CH_2)_5OH$ ----------> tetrahydropyran

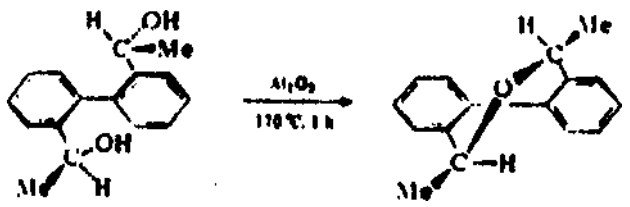
$HO(CH_2)_6OH$ ----------> hexamethylene

M. Iderbert, et al, also of BASF, (Ger. Offen. 2,930,144, 1981) report a similar preparation of cyclic ethers by dehydration of alpha,gamma-diols, but using an organic suspension of aluminum oxide prepared by precipitating alkali aluminate solutions with an acid:

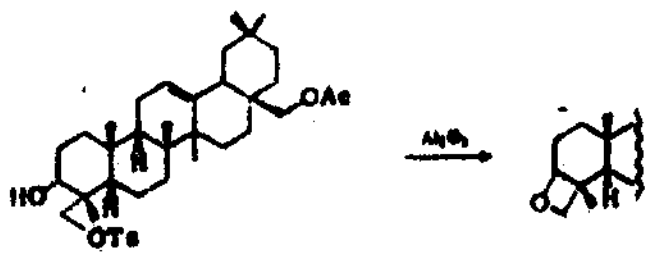
alumina

1,4-butanediol ----------> THF

Posner cites a number of intramolecular substitutions by heteroatom nucleophiles in his Angewandte Chemie article. "Kessler (1968) reported that alumina promoted a stereoselective and concerted (i.e., not ionic) intramolecular substitution of one OH group by a second OH group in the same molecule; it was suggested that the role of the alumina was to facilitate removal of the first OH group as the new ether linkage was being formed."

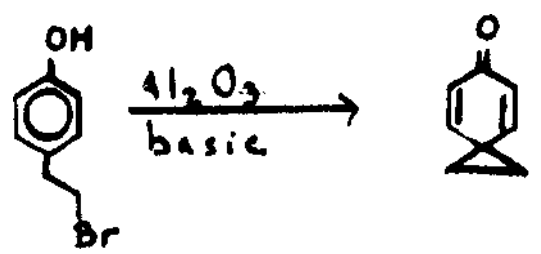


Posner also cites the findings of Tsuda, et al (1975) of an alumina catalyzed, intramolecular substitution reaction with a tosylate leaving group, leading to the formation of a four-membered oxygen heterocycle.

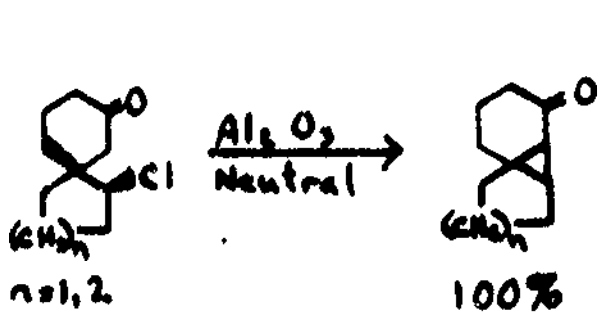


III.A.6.b. Intramolecular Substitution by Nucleophilic Carbon Atoms

Posner cites from the limited literature on intramolecular substitution by nucleophilic carbon atoms, a reaction reported by Baird and Winstein (1957), in which bromide ion is displaced from 4-(bromoethyl)phenol to form the highly reactive spiro-dienone in low yield:

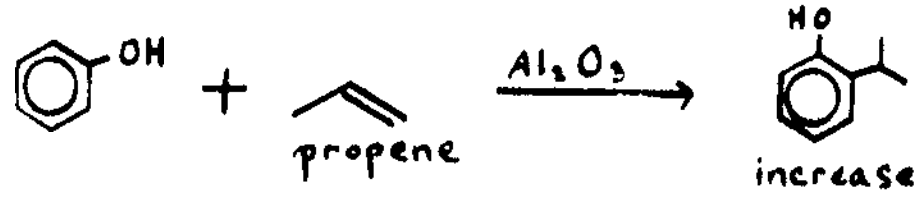


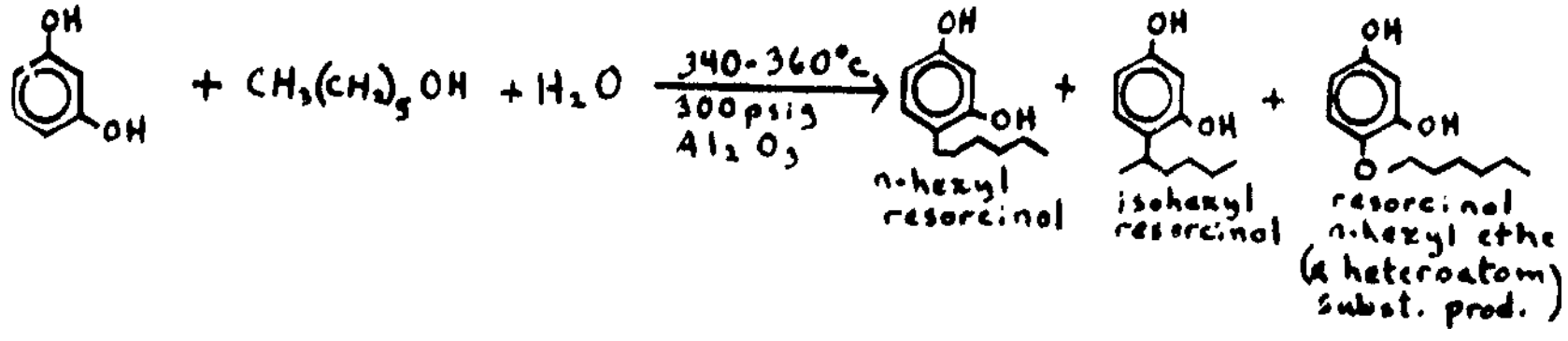
Ruppert and White (1976) reported a highly effective displacement of chlorine from chloro-ketones, by way of alumina-generated enolate ion:

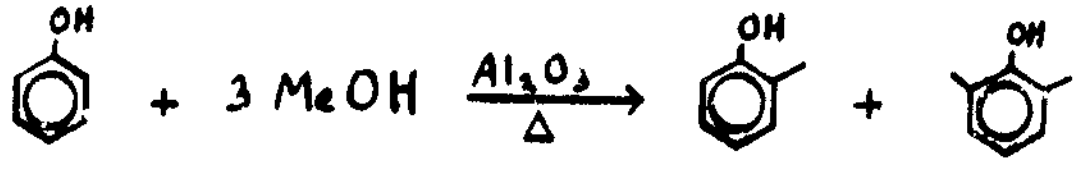


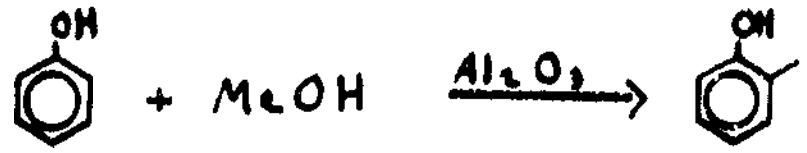
III.A.6.c. Intermolecular Substitution by Nucleophilic Carbon Atoms

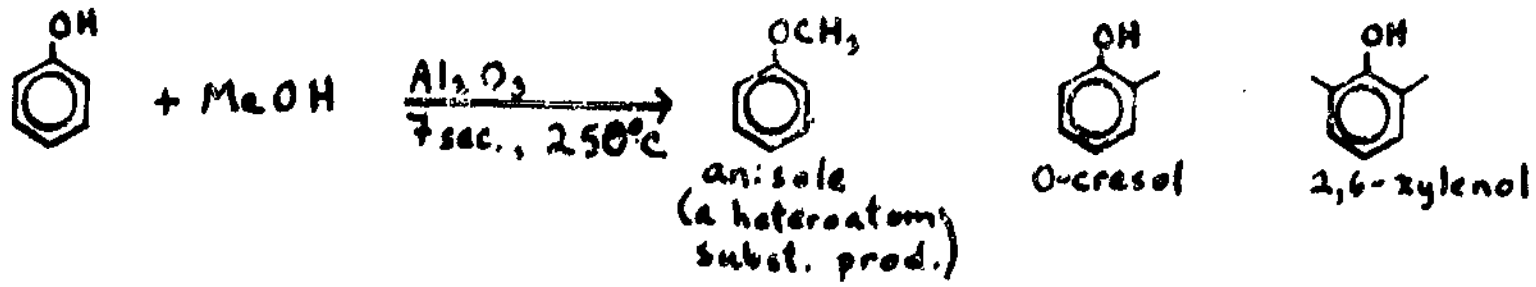
The literature contains many examples of intermolecular substitution by nucleophilic carbon atoms, usually in the form of alkylation or halogenation of substituted ring compounds. In these reactions, alcohol or other ortho, para-directing activating functions such as alkoxy or alkyl groups activate the ortho- and para-positions to be nucleophilic. The alumina surface increases the yield of reactions which in some cases would have taken place even in the absence of a catalyst (Golubchenko et al, 1980; Leach and Starke, 1981, Brit. 1,581,428; Essam and Salvapat, 1963, IN 151,656; Janardanarao et al, 1978; Canavesi, Roberto, et al, 1980, Swiss Patent 620,186)

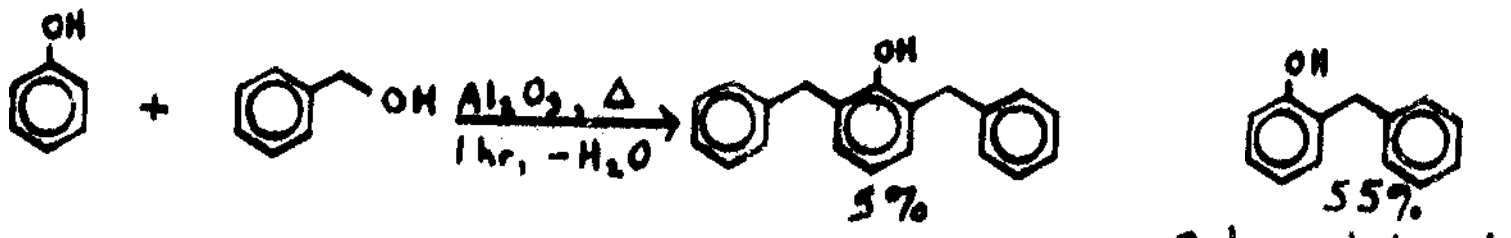

OH
+
propene
Al_2O_3
HO
increased yield


OH
OH
+ $CH_3(CH_2)_5OH$ + H_2O
340-360°C
300 psig
Al_2O_3
n-hexyl resorcinol
isohexyl resorcinol
resorcinol n-hexyl ether
(a heteroatom subst. prod.)

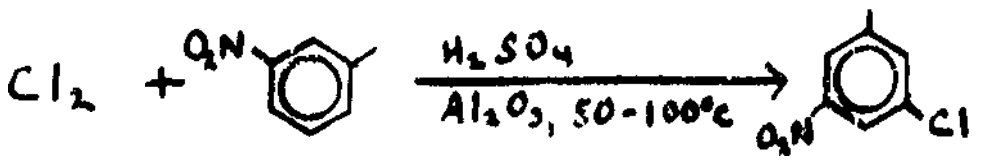

OH
+ 3 MeOH
Al_2O_3
Δ


OH
+ MeOH
Al_2O_3


OH
+ MeOH
Al_2O_3
7 sec., 250°C
OCH_3
anisole
(a heteroatom subst. prod.)
OH
o-cresol
OH
2,6-xylenol

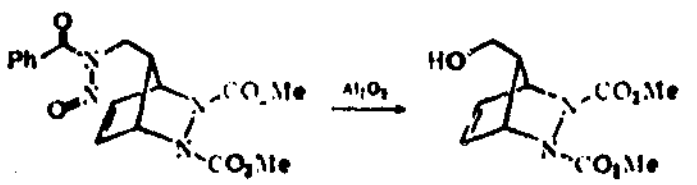

OH
+
OH
Al_2O_3, Δ
1 hr, $-H_2O$
5%
OH
55%
o-benzylphenol

L.J. Pepoy (BASF Wyandotte, 1980, Canadian Patent 1,176,654) reported the following alumina-catalyzed aromatic halogenation which appears to defy the directing groups:

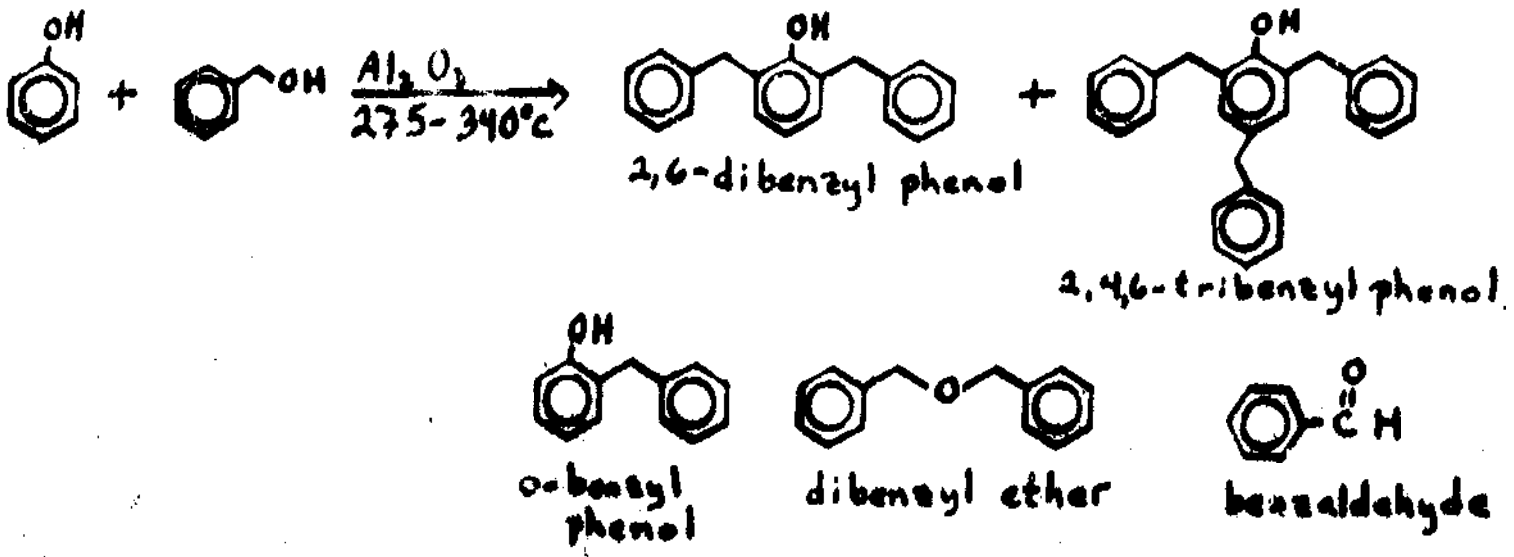


III.A.6.d. Intermolecular Substitution by Heteroatom Nucleophiles

Possibly the most common of the intermolecular substitution reactions by heteroatom nucleophiles is the undesired substitution of an organic function by surface hydroxyl groups during alumina chromatography. Such a reaction is noted by Posner (Trost et al, 1973):



The following alumina-catalyzed reaction, reported by Filbey, Braxton and Meltsner of the Ethyl Corp. (1985, U.S. 4,514,577) involves heteroatom substitution for the ether product, nucleophilic carbon substitution for the benzyl-substituted phenols, and oxidation for benzaldehyde to result in a large array of polyaromatic compounds.



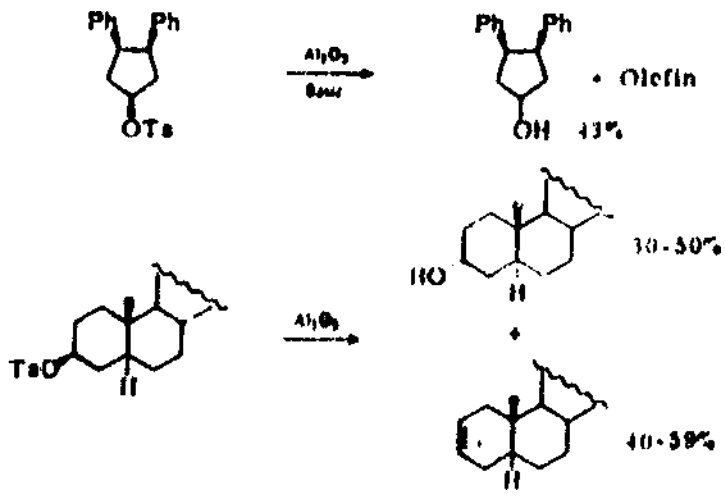
In 1981, Posner (Synth, 1981) reported a simple, mild and convenient method for acetylating prim ..cohols at alumina surfaces:

$$R\text{-}CH_2OH + C_2H_5O\text{-}COCH_3 \xrightarrow[\text{r.t. 1 hr}]{\text{alumina}} RCH_2\text{-}O\text{-}COCH_3$$

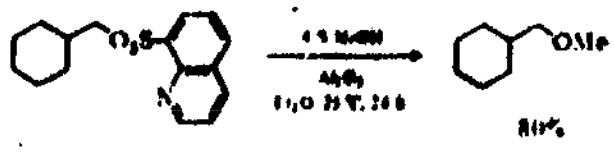
Posner, in conjuriction with Oda (1981), displayed the selectivity of this mild primary alcohol acetylation method by conducting it in the presence of secondary alcohols:

$$R\text{-}\underset{\displaystyle OH}{\underset{|}{CH}}\text{-}CH_2OH \xrightarrow[\text{alumina, 75-80°C}]{\text{EtOAc}} R\text{-}\underset{\displaystyle OH}{\underset{|}{C}}\text{-}CH_2OAc$$

There have been a number of experiments in which surface hydroxy groups cleave and replace specialized leaving groups. The reaction often proceeds to olefin formation due to dehydration (Warshawsky and Fuchs, 1969; Chang and Bilckenstaff, 1958):



Alumina, doped with heteroatom nucleophiles, has also proven to be effective in cleaving and replacing leaving groups: (Posner, Rogers, Kinzig, and Gurria, 1975)



Amine-doped alumina was found to be effective in substitution reactions with aliphatic

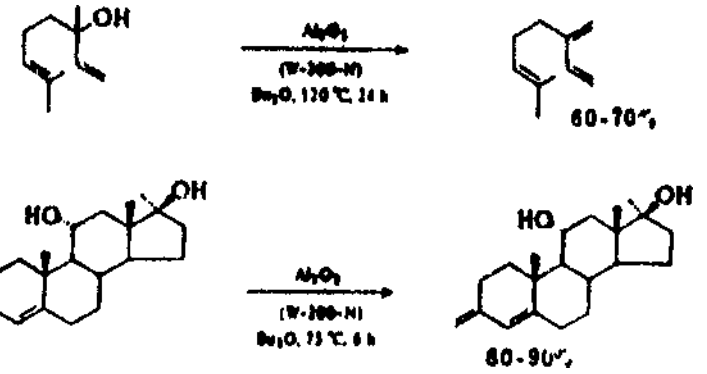
and benzylic halides: (D.Z. Rogers, Ph.D. Thesis, 1977)

$$PhCH_2Cl \xrightarrow[\text{neutral alumina}\\ Et_2O,\ 25^\circ C,\ 48\ hr]{PhNH_2\ (3\ equiv.)} PhCH_2NHPh$$

III.A.7. Elimination Reations

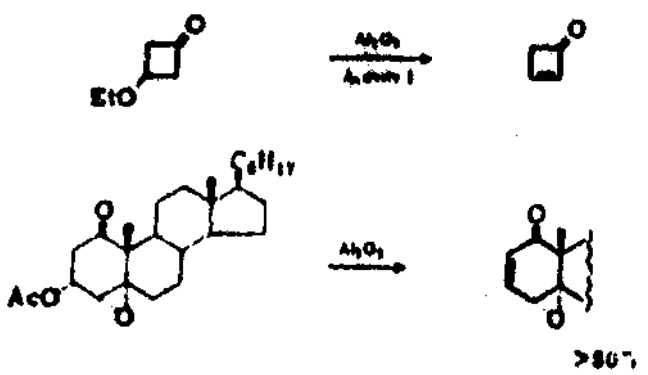
III.A.7.a. Elimination of H-OH from Alcohols

There is limited literature on the dehydration of alcohols under mild conditions. Pines et al (1966) have studied alcohol dehydration in the gas phase, and von Rudloff (1961) studied the dehydration of non-volatile terpine alcohols on pyridine or quinoline doped alumina at temperatures at or above 200°C. These methods have not proven sufficient to allow selective elimination in a diol. Posner and Fehr (unpublished) found that linalool and a steroidal triol undergo dehydration under mild conditions of 75°-120°C in dibutyl ether solvent over Woelm-200-N alumina.

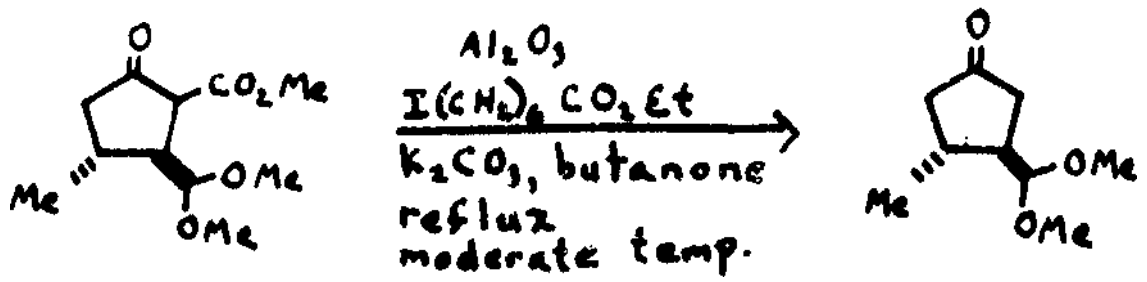


III.A.7.b. Elimination of H-OR and H-O_2CCH_3 from Ethers and Acetates

Ethers and carboxylate esters are usually unreactive toward alumina at room temperature unless the ether or acetate function is located beta to a keto group. (Posner, 1978; Weissenberg et al, 1974)



The following clevage reaction occured alpha to the keto group under milk co. ions (Greene et al, 1976):



III.A.7.c. Deamination

Lycourghiotis, Alexis, and Katsanos (1979) reported the following deamination which proceeds through an intermediate on the alumina surface.

$$R\text{-}CH_2\text{-}CH_2\text{-}NH_2 \xrightarrow{\text{alumina}} R\text{-}CH{=}CH_2$$

III.A.7.d. Elimination of O-Ts from Tosylates

Posner provides an excellent analysis of this area in his 1978 Angewandt Chemie article. There is no need for further elaboration.

III.A.7.e. Elimination of Halogens

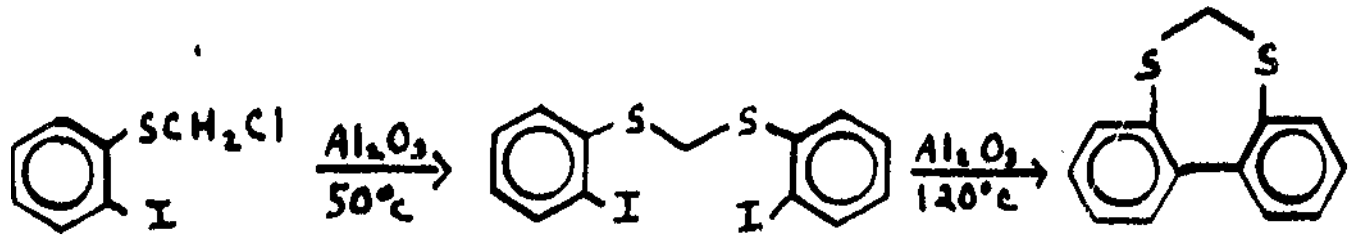
Strobach and Boswell (1971) note that, contrary to circumstances in homogenous liquid phase, dehydrohalogenations, in which alkyl flourides are the least reactive halides, they are the most reactive halides in heterogenous eliminations over alumina. Posner, Gurria, and Babiak (1977) report that 2-iodooctane is stable toward Woelm-200-N alumina for 24 hours at room temperature, while 1,1-difluorocycloheptane undergoes elimination to 1-flourocycloheptane.

Most alumina catalyzed dehydrohalogenations reported occur under relatively harsh conditions (Mochida et al, 1978; Asahi-Dow, 1981, JP 80 87,729)

$$Cl_2CHCH_2Cl_{(steam)} \xrightarrow{\text{alumina, 900°C}} CH_2{=}CCl_2$$

$$ClCH_2CHCl_2 \xrightarrow[N_{(g)} \text{ or } CH_2CHCl]{\text{alumina, 375°C}} CH_2{=}CCl_2$$

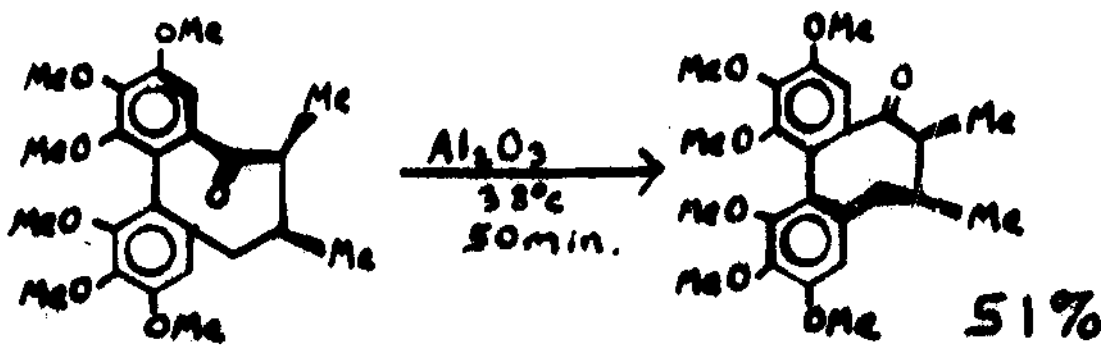
The following mild alumina-catalyzed reaction of arylthialkyl halides involves a final elimination step which does not occur in the abscence of alumina (Jigajinni, Wightman, and Campbell, 1981)



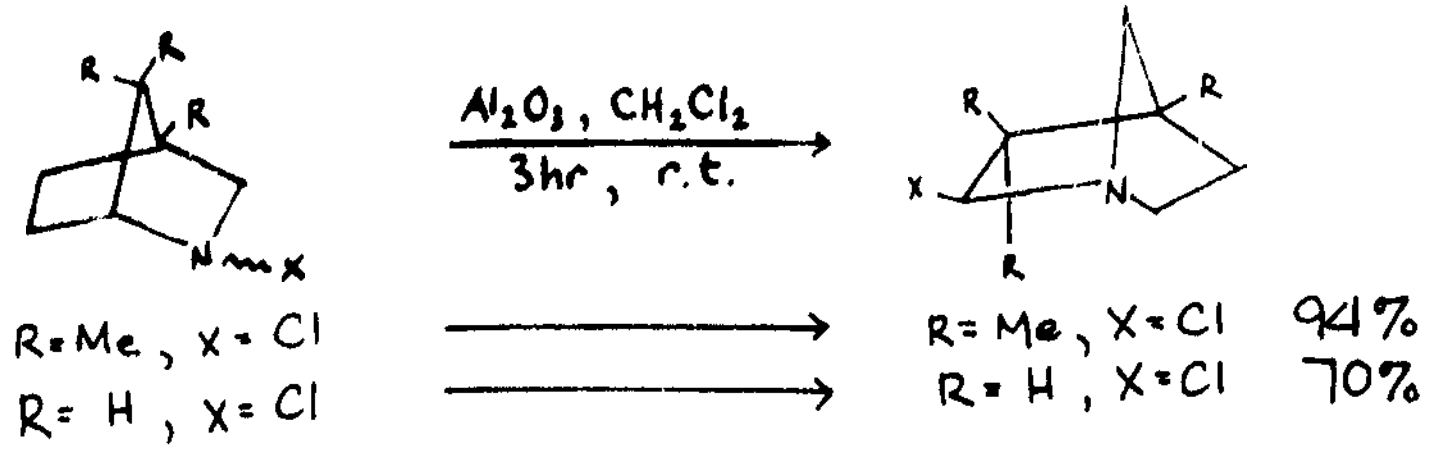
o-iodophenyl chloro-methyl sulphide

III.A.8. Rearrangements

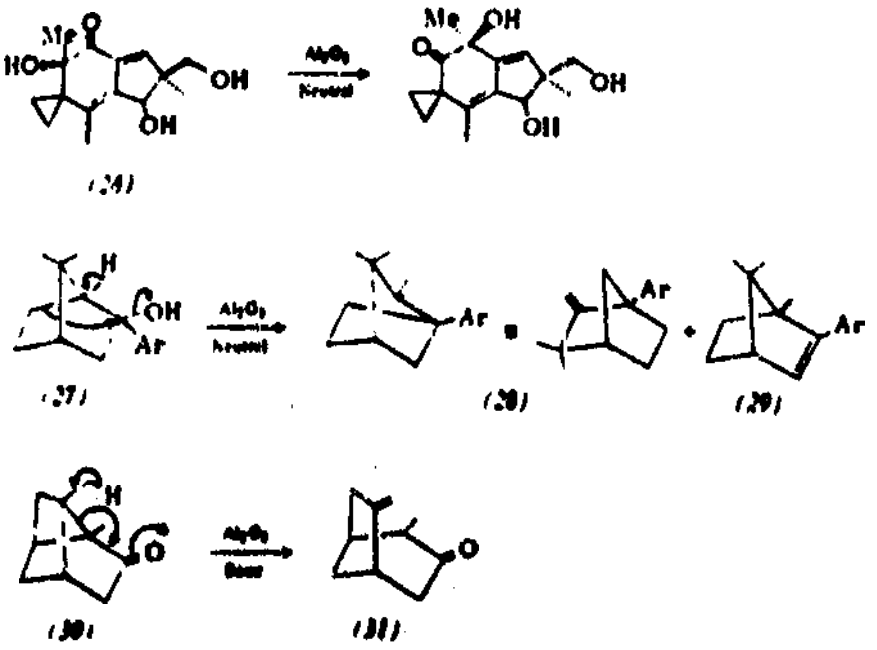
Alumina has been found to reduce rotational barriers by up to 15.5 Kcal/mol in some bridged biphenyls, allowing conformational inversion under mild conditions. (Mervic et al, 1979)



There has been substantial research on alumina-promoted skeletal rearrangements in the nor-bornyl system and other strained N-chloroazabicycles (Davies et al, 1985).



Posner notes several interesting skeletal rearrangements facilitated by alumina (Ichihara and Matsumoto, 1978; Hughes et al, 1971; Wolff et al, 1957).



III.B. Aqueous Chlorine Chemistry

Chlorine gas, used in most American water treatment facilities, hydrolyzes almost completely in the following fashion (Voudrias, Ph.D. thesis, 1984):

$$Cl_{2(g)} \longleftrightarrow Cl_{2(aq)} \qquad K_h = 6.2 \times 10^{-2}\ (25^{\circ}C)$$

$$Cl_{2(aq)} + H_2O \quad <=====> \quad HOCl + H^+ + Cl^- \qquad K_h = 4 \times 10^{-4} \quad (25^oC)$$

HOCl dissociates according to the following reaction (Voudrias, Ph.D. thesis, 1984):

$$HOCl \quad <=========> \quad H^+ + OCl^- \qquad pK_a = 7.5 \ (25^oC)$$

The sum of $Cl_{2(aq)}$, OCl^-, and HOCl is known as free chlorine residual (Snoeyink and Jenkins, 1980)

The source of free chlorine in the following experiments was calcium hypochlorite $Ca(OCl)_2$, which dissociates by the following reaction:

$$Ca(OCl)_2 \quad <=========> \quad Ca^{++} + 2OCl^-$$

Free chlorine reacts with phenol as Cl^+, the hydroxyl group being displaced from HOCl (Morris, 1978).

III.B.1. Reactions of Chlorine with Organic Compounds:

Chlorine can react with organic compounds by three mechanisms (Jolley et al, 1978)

1) Double bond addition
2) Oxidation
3) Substitution of chlorine for another substituent on the organic molecule.

Trihalomethanes have been the subject of a great deal of water treatment chemistry research. In addition, chlorinated organic compounds such as chlorophenols, and oxidation products such as quinone are formed during water treatment (Voudrias, Ph.D. thesis, 1984). Between 0.5% and 5% of chlorine used goes to haloform reactions, 50-80% to organic oxidation to CO_2, 0-5% to haloacetonitrile formation, 1-6% to non-haloform organic halogen, approximately 0.1% to halogenated phenol formation, and the remainder to other reactions (Hileman, citing Sean, 1982)

III.C. Organic Compounds in Natural Waters

Natural waters contain a wide array of organic compounds which are of relevance to water treatment chemistry. Many of these result from natural color-producing humic materials which are present in natural waters in various concentrations. The core structure of these humic materials appears to be several phenols and phenolic acids (resorcinol, catechol, vanillic acid, syringic acid, 3,5-dihydroxybenzoic acid, p-hydroxybenzoic acid) (Schmitzer and Khan, 1972). These phenolic materials are apparently the precursors of such undesirable taste and odor producing compounds as chlorophenols, which are found in chlorinated waters. 4-chloro-, 2,4-dichloro-, and 2,4,6-trichlorophenols were found to result from the aqueous chlorination of p-hydroxybenzoic acid, a degradation product of humic substances (Larson and Rockwell, 1973)

IV. MATERIALS AND EXPERIMENTAL METHODS

IV.A. Materials

Calcium hypochlorite (Fisher Scientific), $Ca(OCl)_2$, the source of free chlorine, was dissolved in deionized water to achieve an OCl^- concentration of 5ppm, similar to that used in drinking water treatment.

The French manufacturer, Rhome-Poulenc Aubervilliers, provided activated aluminum which goes by the commercial name, GFSC. It comes in extruded form with a particle size of 0.8-1.2 mm^2, and has a BET surface area of 200 m^2/g. For this experiment, the particles were pulverized using a mortar and pestle in order to maximize surface area.

2,4-dichlorophenol (2,4-DCP) was the organic compound used. It can be present in chlorinated natural waters, as a result of chlorination of phenol from lignin, as stated in III.C.

IV.B. Batch Reactions

Batch reactor tests were used to determine the products of the free chlorine-dichlorophenol reactions both with and without aluminum oxide. Control I was run at a pH between 6.0 and 7.0. Enough 2,4- dichlorophenol was dissolved into one liter of deionized water to create a 5 ppm solution. An equal molar amount of OCl^- from $Ca(OCl)_2$ was then added to the solution. The solution was allowed to react for one hour at room temperature, while being stirred magnetically. After the reaction time, excess chlorine was destroyed with $NaSO_3$, after acidification to pH 3 with H_2SO_4.

In the experimental reactions, the reaction was performed identically, except that one gram of pulverized aluminum oxide was added to the liter reaction vessel after the addition of dichlorophenol and before the addition of $Ca(OCl)_2$. Reaction time for Trial I was two hours rather than one. Trial II was allowed a one hour reaction time. A second control (Control II) in which unreacted alumina was extracted was conducted to ensure that compounds identified were not already present on the catalyst.

IV.C. Product Analysis

For Control I, a liquid-liquid extraction with three 20 ml portions of methylene chloride was performed following the reaction quenching. The methylene chloride was then concentrated approximately 25x under a stream of high purity nitrogen gas. For Control II, one gram of pulverized aluminum oxide, of the type used in the experimental reactions, was soxhlet extracted for 24 hours in 250 ml of methylene chloride. The extract was concentrated 250x and analyzed as in the experimental reactions.

Following the experimental reactions, the aluminum oxide was removed by vacuum filtration through a .45 micron membrane filter. The filtrate was then liquid-liquid extracted with three 20 ml portions of methylene chloride. The extract was concentrated as above.

The aluminum oxide was retrieved from the membrane filter and soxhlet extracted for 24 hours in 100 ml of methylene chloride. This extract received closest analysis, and was concentrated in a Kuderna-Danish evaporative concentrator between 166 and 350 times in various repetitions of the experiment. In Trial I, it was necessary to heat the hot water bath in which the K-D concentration apparatus was placed to 95°C, well above the boiling point of methylene chloride. This was because the apparatus could not be submersed deeply enough in the water bath (see figure 1). The rising gas bubbles were therefore cooled as they rose through the cooler methylene chloride above. This greatly impeded evaporation. To have concentration occur at a reasonable rate, it was necessary to raise the bath temperature substantially. In the subsequent Trial II, the K-D concentration apparatus was lowered into the hot water bath to a depth slightly greater than the level of the methylene chloride (see figure 2). This created much greater uniformity of temperature in the solvent, allowing the concentration to proceed with a bath temperature only slightly higher than the $MeCl_2$ boiling temperature.

Concentrated extracts were kept in the freezer between the time of concentration and the time of analysis in order to prevent compounds formed from breaking down and to prevent any further reactions. A third trial was conducted, but the extracts were left unrefrigerated for one week after concentration. As expected, few compounds were identified in the analysis. Consequently, the results of this trial are not included in

the following.

The concentrated organic extracts were analyzed on a Hewlett-Packard 5985 gas chromatography/mass spectrometer (GC/MS). Two µl of each concentrate was injected into a 20 meter SP-2100 glass or DB-1 30m fused silica capillary column (J and W Scientific, Inc., Orangevale CA). The column was programmed from 40°C with a 5 minute hold to 240°C at a rate of 5°C/minute. When possible, compounds were identified by comparing the mass spectra with those in the Eight Peak Index (1974), the Registry of Mass Spectral Data (1974), the EPA/NIH Mass Spectral Data Base (Heller and Milne, 1978, supp. 1980), or existing literature. In most cases these sources were inadequate and we were forced to identify compounds tentatively by direct interpretation of the mass spectral fragmentation patterns.. Only qualitative (not quantitative) analyses were performed.

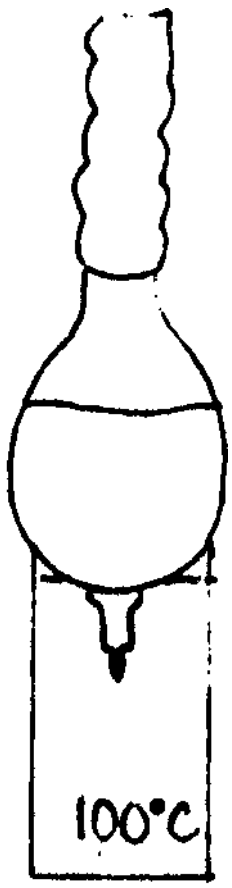


Figure 1
Condensation Apparatus
Trial I

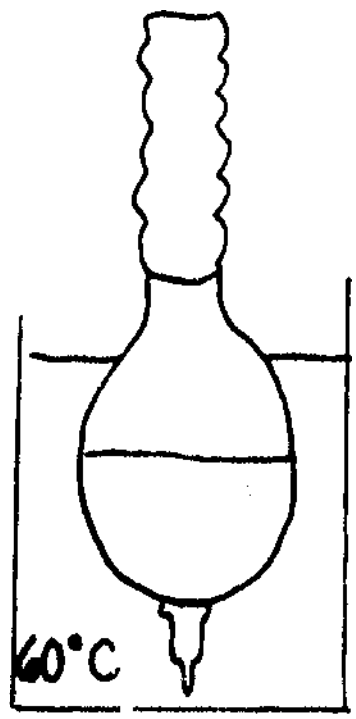


Figure 2
Condensation Apparatus
Trial II

V. RESULTS AND DISCUSSION

V.A. Results

Free chlorine and 2,4-dichlorophenol reacted in the aqueous control batch reaction without Al_2O_3 (Control I) to yield a mixture of 2,4-dichlorophenol and 2,4,6-trichlorophenol, as expected. The compounds were easily identifiable from the literature.

Control II, the methylene chloride soxhlet extraction of unreacted Al_2O_3, showed only two low molecular weight aliphatic compounds, five phthalate varieties, and three low molecular weight compounds which were unidentified. No chlorinated compounds were found. None of the compounds identified in Control II would be expected to interfere with the analysis of the experimental reactions.

When the reaction was conducted in the presence of Al_2O_3, however, many additional products appear to have been formed. Unfortunately, results were not entirely conclusive since many of the products identified were not formed reproducibly in repeat runs, and many of the products could only be identified tentatively.

Compounds identified in all experimental reactions are listed in order of retention time in Table 1. The plurality of compounds were found in the methylene chloride soxhlet extract of the aluminum oxide catalyst (designated by "A" in Table 1), indicating that they were adsorbed to the alumina surface. A significant array of compounds were present in the aqueous layer (designated by "W" in Table 1), free of the alumina surface. These compounds were isolated by liquid-liquid extraction using methylene chloride.

The full ion chromatographs of both of the trials of the experimental reaction are shown in figure 3 (Trial I, aqueous layer) and figure 4 (Trial II, aqueous layer). The total ion chromatograph for the soxhlet extract of Trial I is shown in figure 5. In Trial II, two full scan GC/MS runs were conducted, one concentrated 200x and one 350x. Both chromatographs are shown in figures 6 and 7 respectively. The peak numbers listed in Table 1 correspond to the numbered peaks on the chromatographs. The mass spectra for all of the numbered compounds are displayed in figures 8 through 32 in the

Appendix along with their respective peak numbers. Most of the unnumbered peaks correspond to either phthalates, low molecular weight aliphatic compounds, or silicone compounds resulting from a lubricant used.

TABLE 1

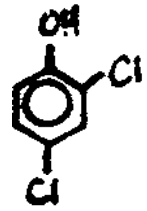
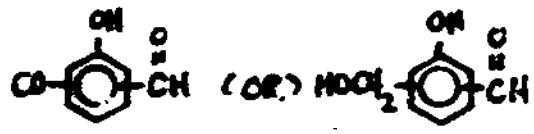
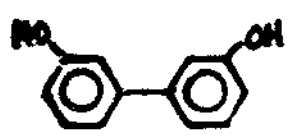
Peak #	Retention Time	Structure	Name	Molecular Weight	Identification Trial I	Identification Trial II
1	14.8		2,4-dichlorophenol	162	U	U
2	15.4		methoxysalicylaldehyde or salicylaldehydebenzyl alcohol	152	A	
3	20.2		2,4,6-trichlorophenol	196	U	U
4	21.6-23.2		2,2'-diphenol	186	A	
5	24.7	[illegible]		220		A
6	27.1-28.3		2-phenoxy phenol	186	A/U	

TABLE 1 continued

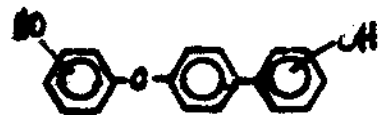
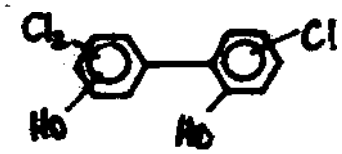
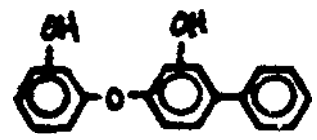
Peak #	Retention Time	Structure	Name	Molecular Weight	Identification Trial I	Trial II
7	34.7, 35.9	UNKNOWN		256		A
8	34.8-38.8		phenol biphenylol ether	278	U	
9	36.3		trichlorodihydroxy biphenyl	288	A	U
10	38.4	UNKNOWN		284		A
11	38.8	UNKNOWN		312		A
12	39.8	UNKNOWN		278	A	
13	40.5		phenol biphenylol ether	278	A/U	
14	40.6	UNKNOWN		276	U	

TABLE 1 continued

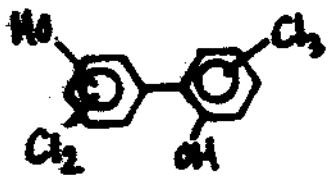
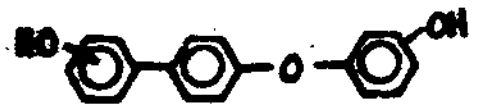
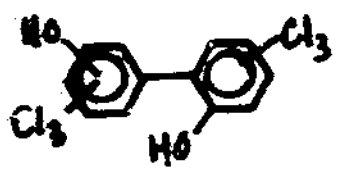
Peak #	Retention Time	Structure	Name	Molecular Weight	Identification Trial I	Identification Trial II
15	41.9		pentachlorobiphenyldiol	356	A	
16	42.2	UNKNOWN		340		A
17	42.6-42.8		phenol biphenylol ether	278	A	
18	43.0	UNKNOWN		334	A	
19	43.7-44.0	UNKNOWN		278	A	
20	43.9	UNKNOWN		316	A	
21	44.7	UNKNOWN		268	A	
22	45.1		hexachlorobiphenyldiol	390	A	

TABLE 1 continued

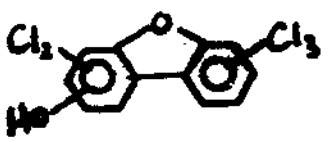
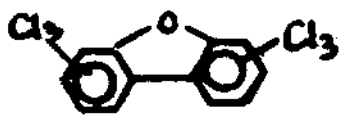
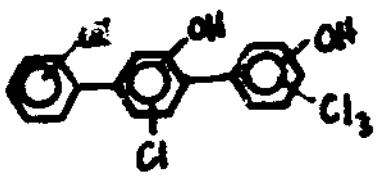
Peak #	Retention Time	Structure	Name	Molecular Weight	Identification Trial I	Identification Trial II
23	45.7		pentachlorodibenzofuranol	354	A	
24	46.1		hexachlorodibenzofuran	372	A	
25	56.8		tetrachlorotriphenol	414	A	

FIGURE 3: Trial I, aqueous layer, part 1

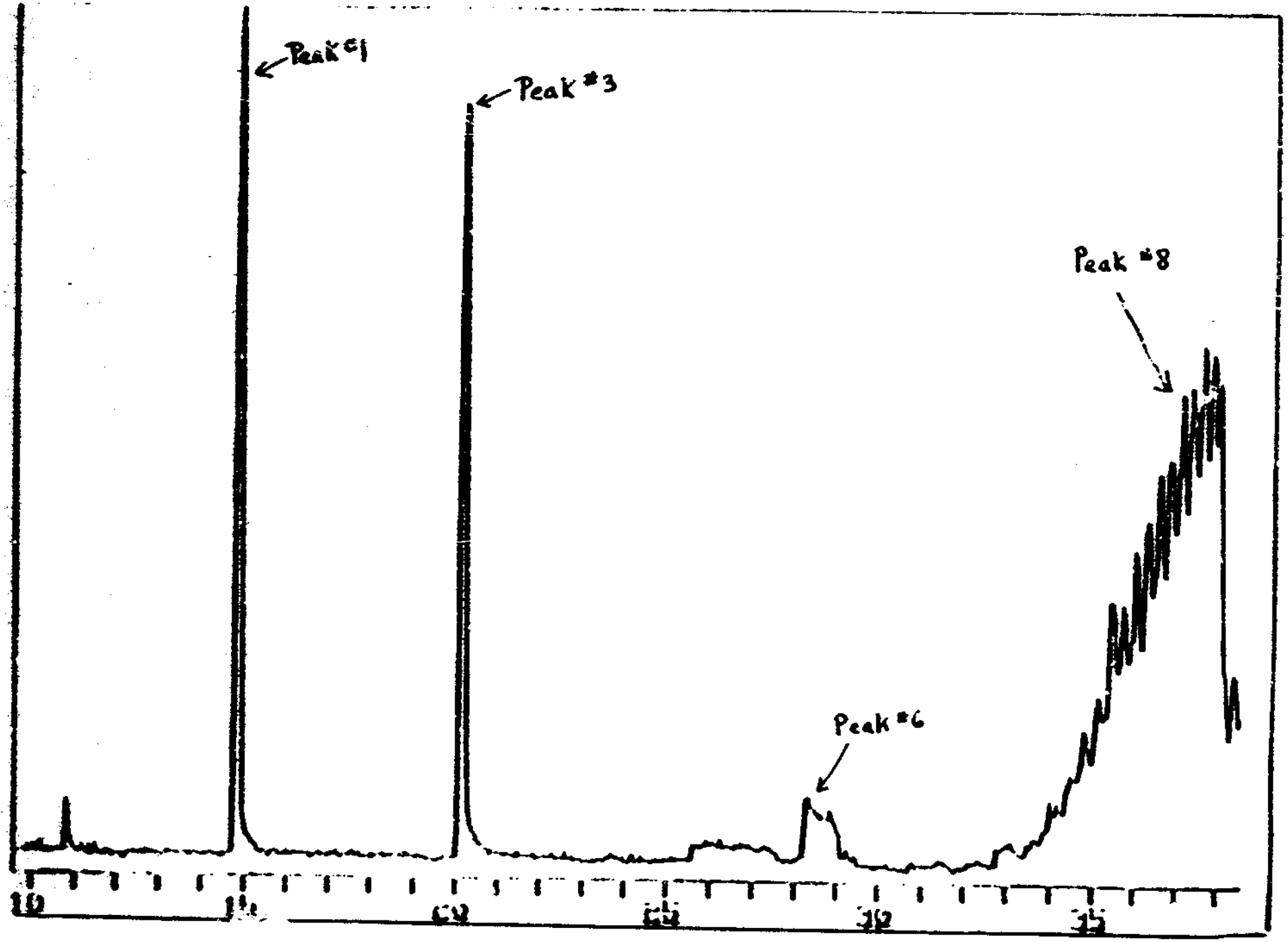


FIGURE 3: Trial I, aqueous layer, page 2

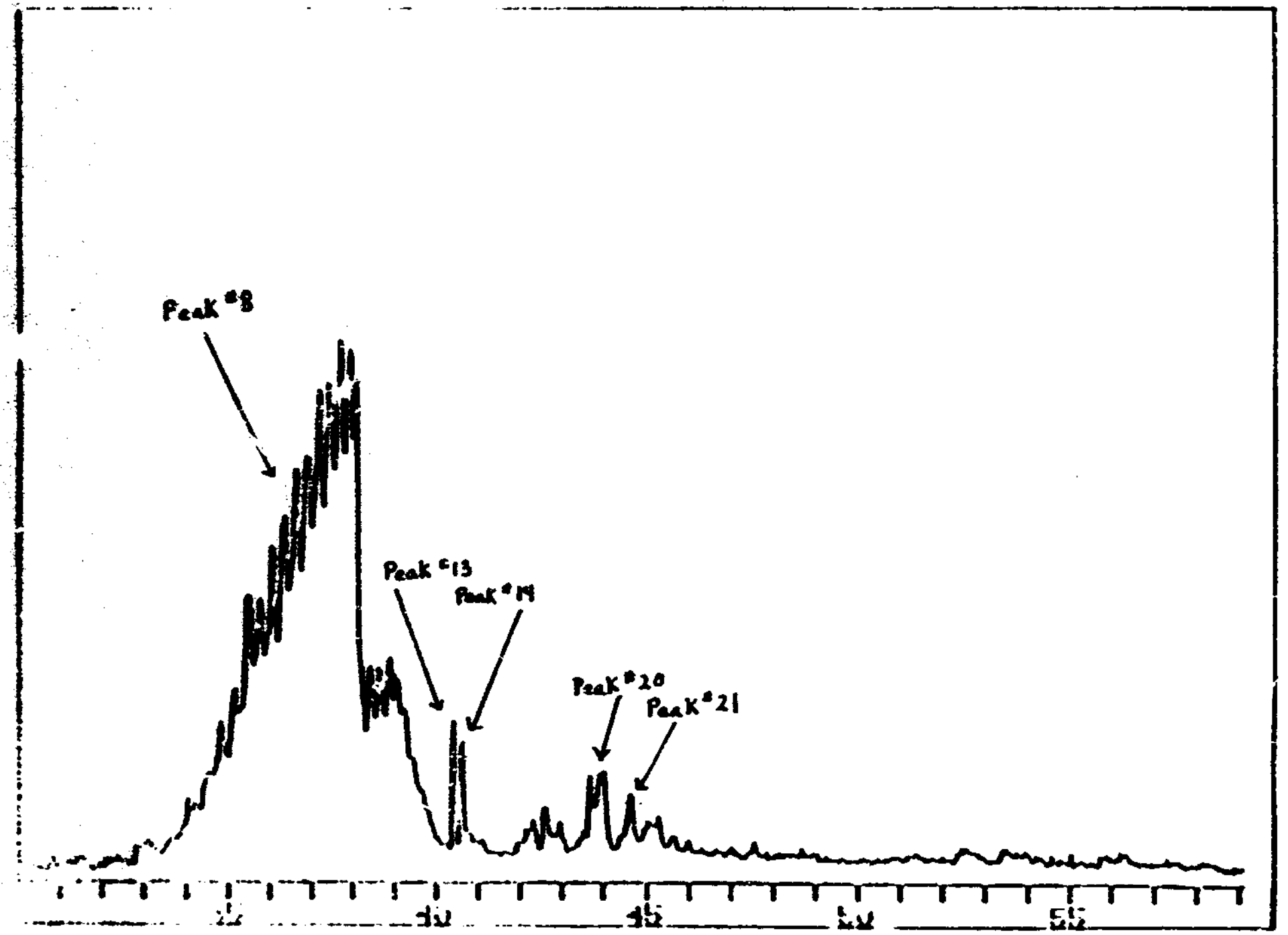


FIGURE 4: Trial II, aqueous layer, page 1

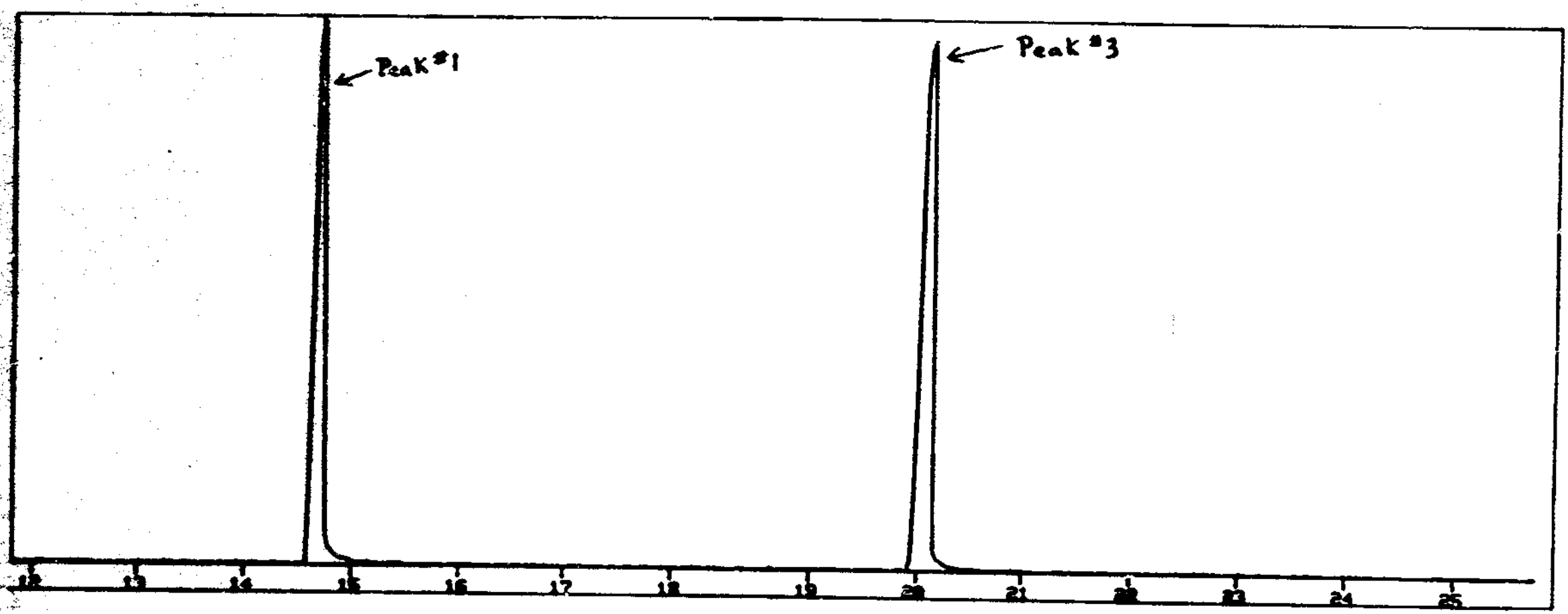


FIGURE 4: Trial II, aqueous layer, page 2

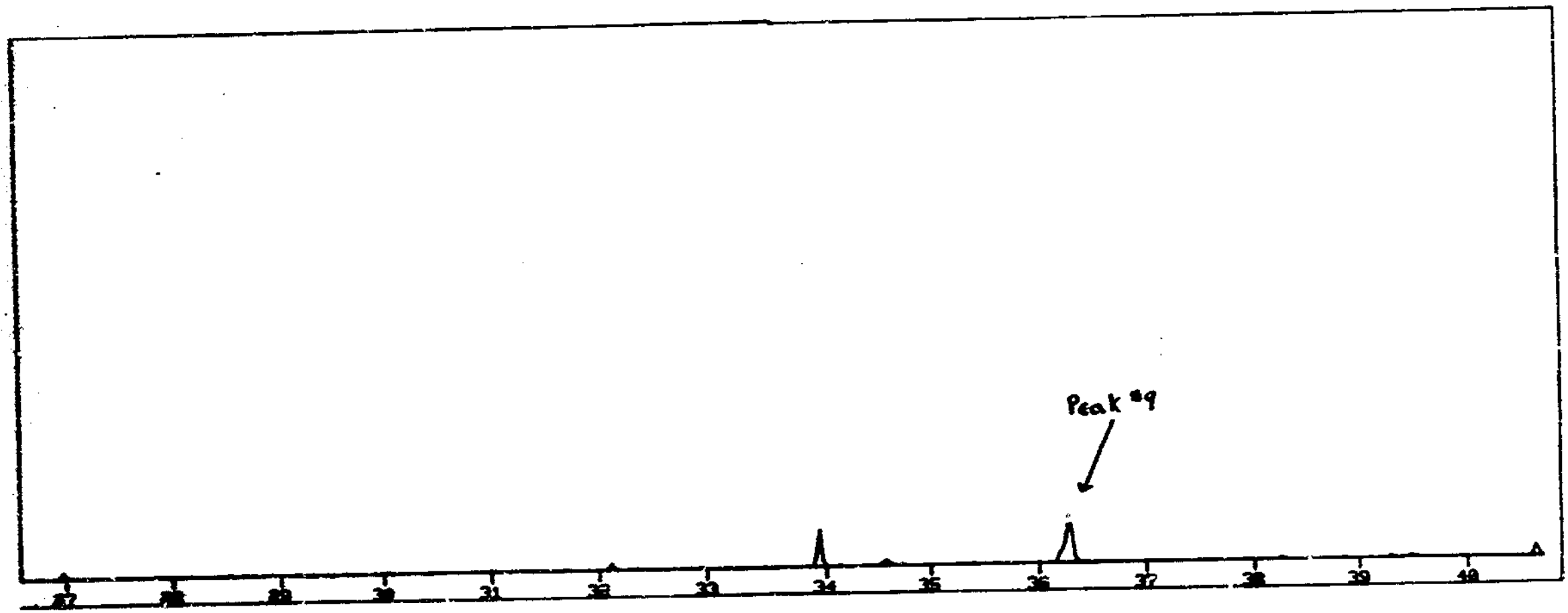


FIGURE 4: Trial II, aqueous layer, page 3

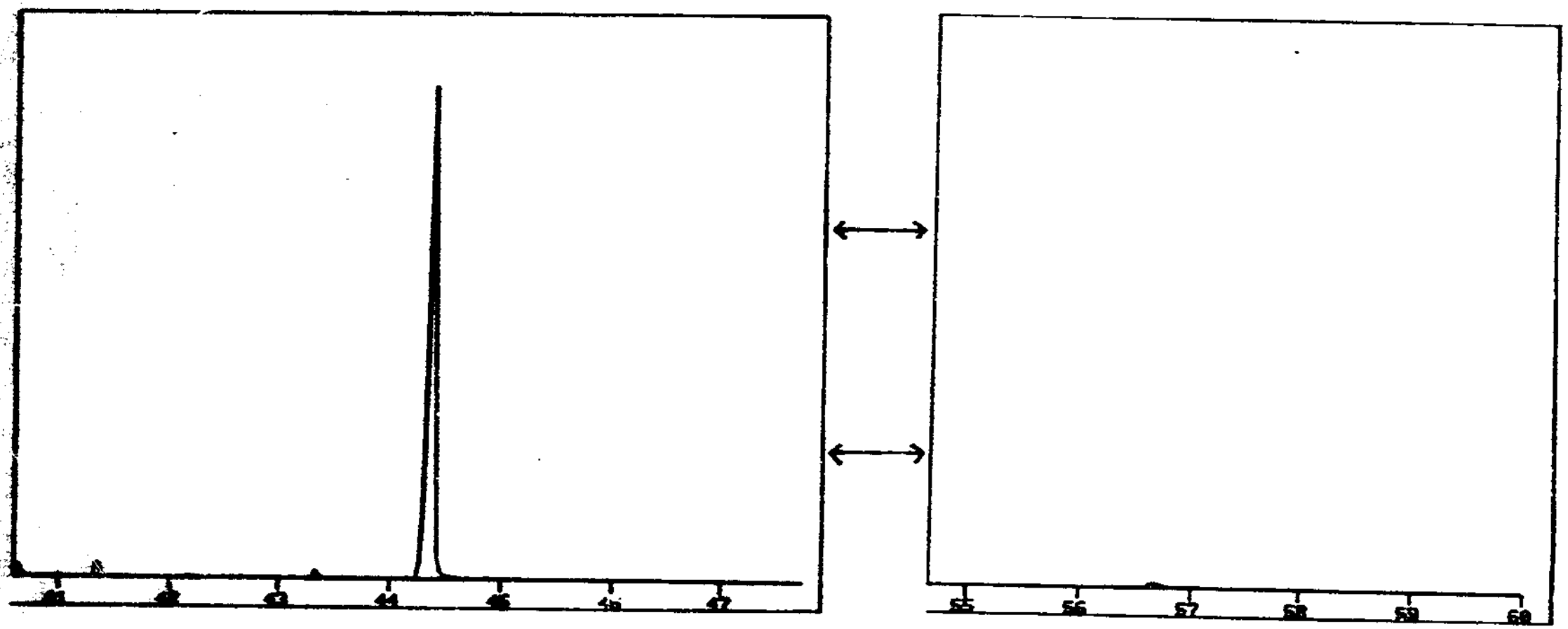


FIGURE 5: Trial I, soxhlet extract, concentrated 75x

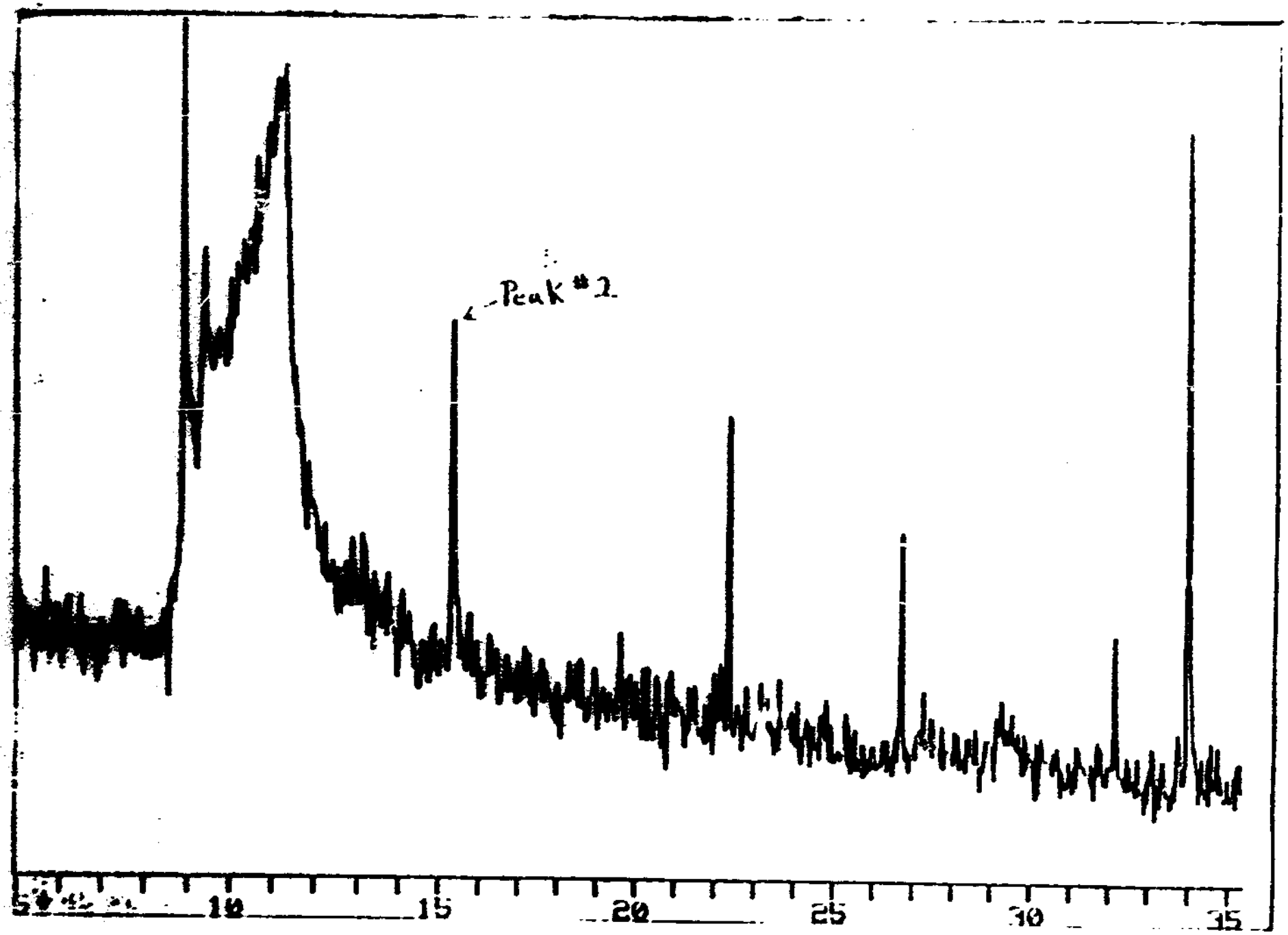


FIGURE 5: Trial I, soxhlet extract, concentrated 166x, page 1

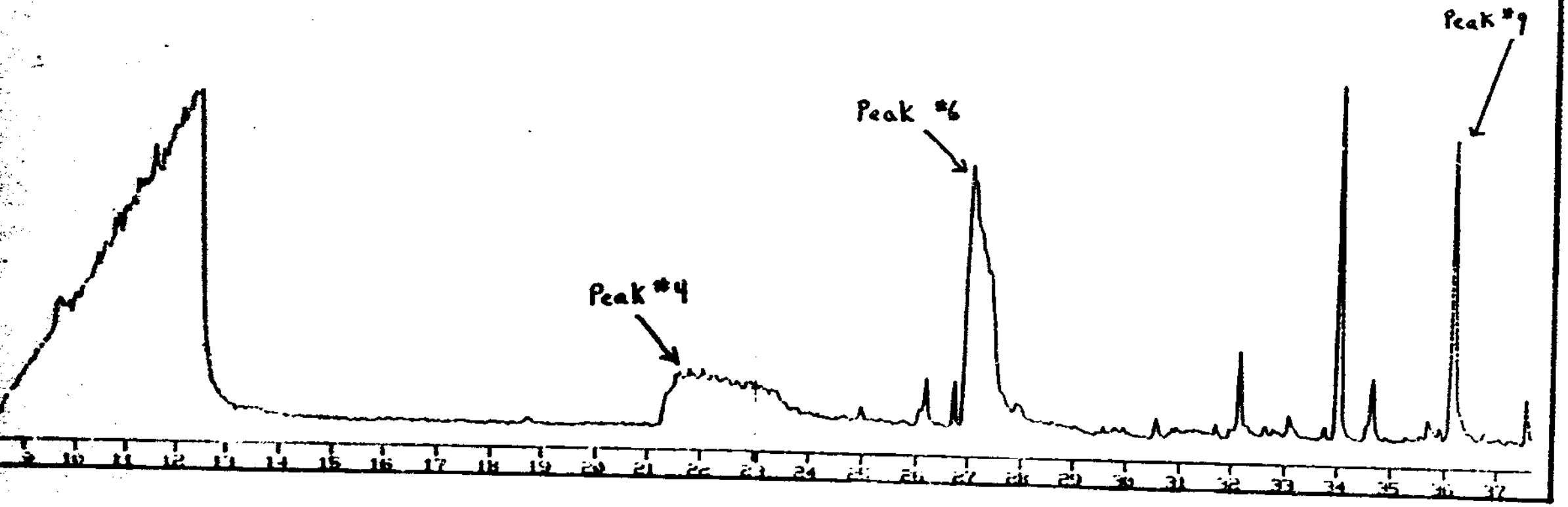


FIGURE 5: Trial I, soxhlet extract, concentrated 166x, page 2

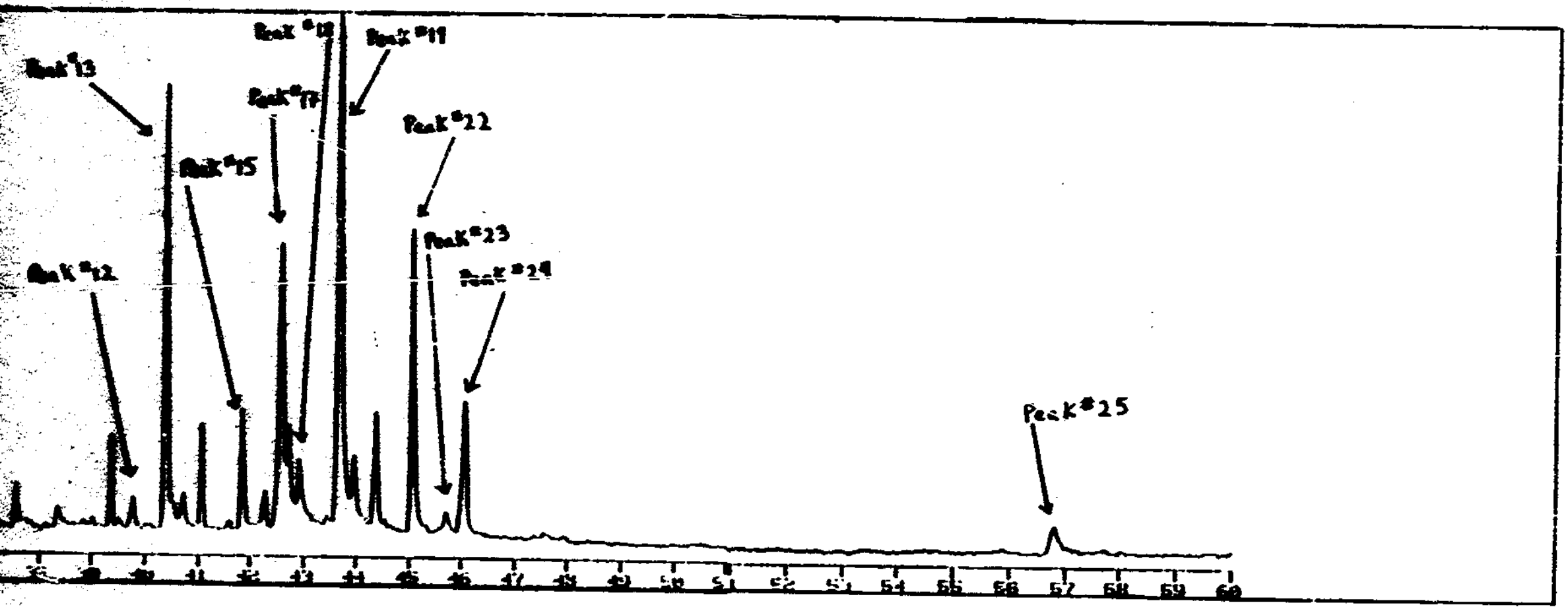


FIGURE 6: Trial II, soxhlet extract, concentrated 200x

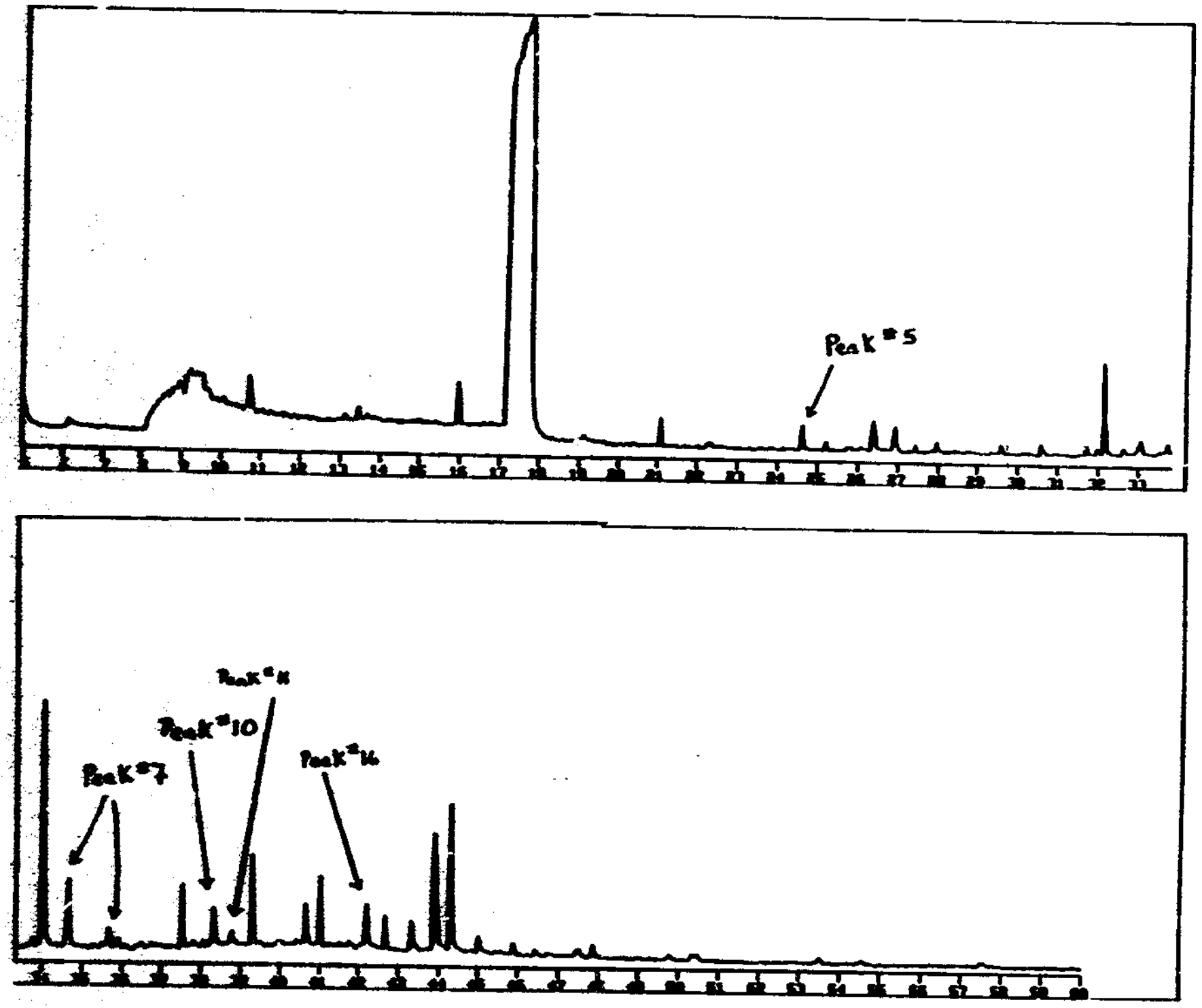
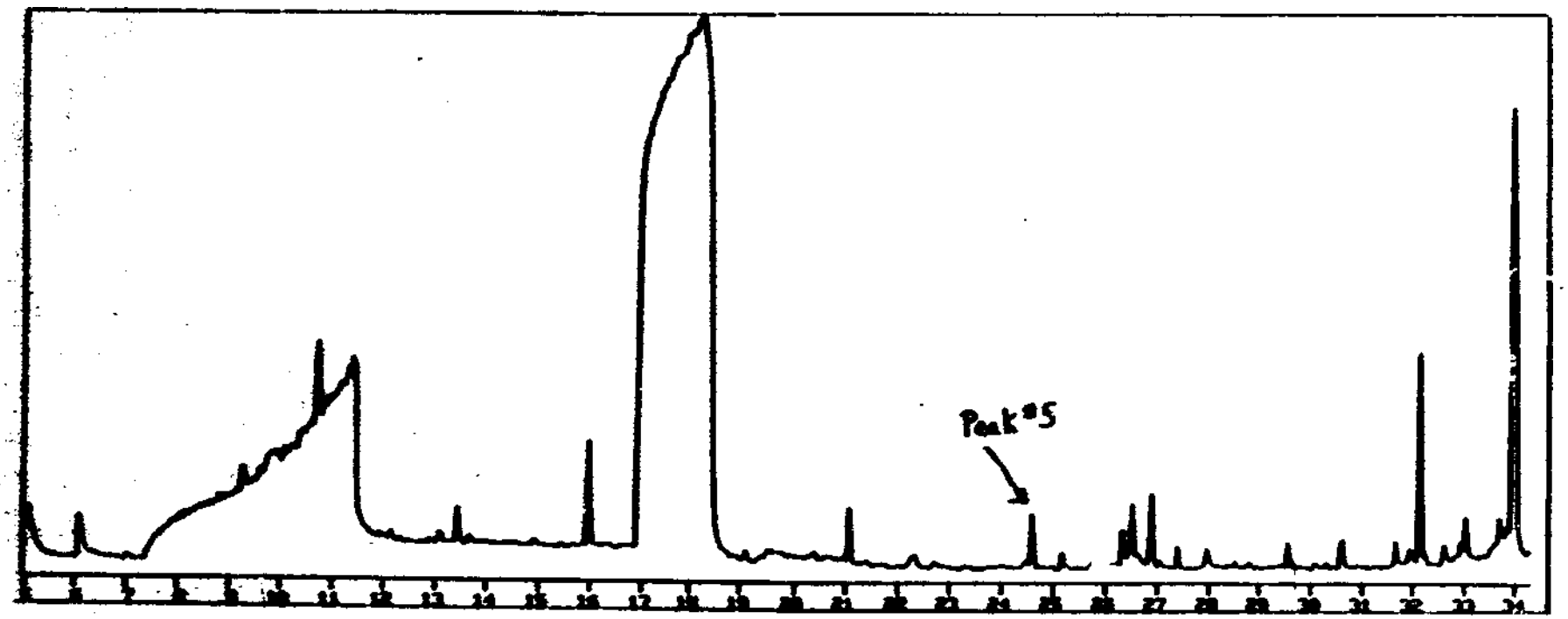
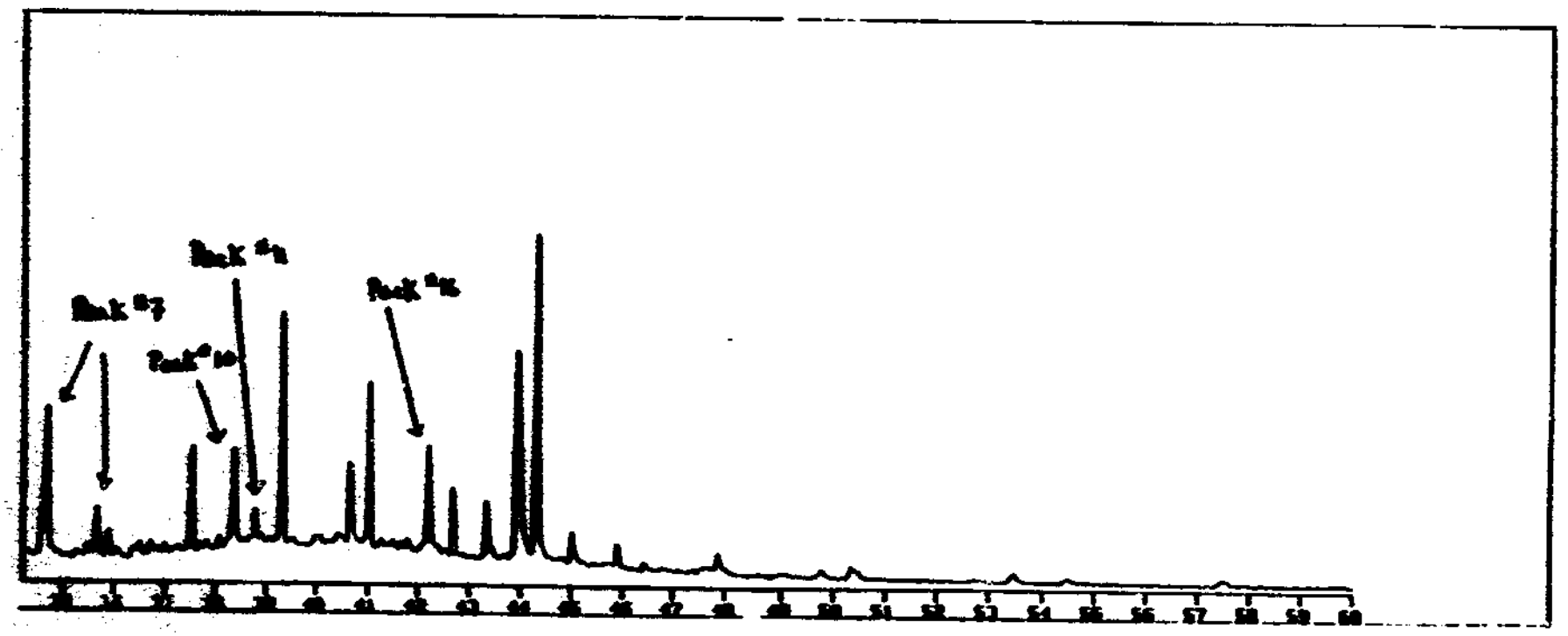


FIGURE 7: Trial II, soxhlet extract, concentrated 350x





V.B. Discussion

Table 1 shows quite clearly that a wide variety of compounds were formed in the presence of Al_2O_3 in addition to the DCP and TCP that are identified in the uncatalyzed reaction. Also immediately noticable from Table 1 is the marked difference between Trials I and II. A far greater number of compounds were identified in Trial I than in Trial II, and most of the compounds identified in Trial II were not found in Trial I. The only compounds identified in both Trials were 2,4-dichlorophenol, 2,4,6-trichlorophenol, trichloro dihydroxy biphenyl, and a compound tentatively identified as a tetrachlorotriphenylol. Of the five compounds found in Trial II that were not found in Trial I, none could be positively identified. Two of the compounds were tentatively identified as fatty acids, one as an ester.

Three factors may explain why such a variety of compounds were formed in Trial I, but not in Trial II: 1) reaction time; 2) free chlorine concentration; 3) heat of hot water bath during concentration.

Factor #1, reaction time, is the most obvious of the three. Trial I was allowed two hours before the reaction was quenched. Trial II had only a one hour reaction time. Obviously more compounds can be formed given a longer reaction time.

The second factor, free chlorine concentration results from the time lag between the two Trials. Trial I was conducted eight months before Trial II (one Trial came between them, but was disgarded for reasons stated earlier). Trial I was conducted using a previously unopened bottle of calcium hypochlorite, $Ca(OCl)_2$. Trial II used that same bottle of $Ca(OCl)_2$, which had by then been exposed to the air on many occasions. Calcium hypochlorite is known to release free chlorine to the air over time, thereby becoming less active, loosing its oxidizing capability. Thus, although an identical amount of $Ca(OCl)_2$ was weighed out for Trial I and Trial II, the concentration of free chlorine was lower in the later reaction. This could partially explain why far fewer chlorination and oxidation products are present in Trial II relative to Trial I.

The third factor, heat of hot water bath during concentration, is most likely the least important. For reasons discussed in the "Products Analysis" section above, the hot water bath was at a substantially higher temperature during the concentration step

in Trial I than in Trial II. While the methylene chloride extract being concentrated could not have been heated above its boiling temperature, the glass of the concentration vessel must have been between the temperature of the 95°C water bath and the boiling methylene chloride. Molecules coming in contact with the glass surface would have experienced a higher temperature in Trial I than in Trial II, and would thereby have been imparted more energy. The additional energy may have allowed certain reactions to occur in Trial I which could not occur in the lower energy of Trial II. These additional reactions would not have involved alumina, since the material had already been filtered out of solution. Nor would they have involved free chlorine, since the reaction had already been quenched. If any such, "added energy" reactions occurred, it was as a result of interactions of compounds already in solution before the reaction quenching. Again, this third factor is highly hypothetical, the reaction time and free chlorine concentration seeming far more significant. Factors 2) and 3) could also explain why products were found in trial II and not in I. Lower chlorine concentrations may have allowed competing reactions. More heat in trial I may have destroyed certain compounds.

V.C. Identification

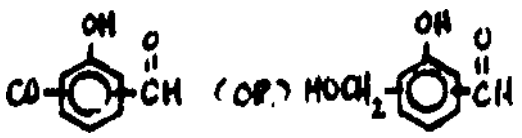
As stated above, all compounds were identified by GC/MS. Where possible, mass spectra were compared to those in the Eight Peak Index (1974), the Registry of Mass Spectral Data (1974), the EPA/NIH Mass Spectral Data Base (Heller and Milne, 1978, supp. 1980), or the existing literature. In most cases, these sources were inadequate, and it was necessary to identify compounds tentatively by direct interpretation of mass spectral fragmentation patterns. This type of interpretation has obvious limitations, especially since none of the compounds were identified in methylated samples. This last fact makes it difficult or impossible to distinguish many ether functions from alcohols. Explanations of interpretations follow.

Peak #1: 

2,4-dichlorophenol was found in Control I, and in the aqueous layers of both Trials I

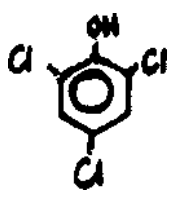
and II. Identification was made by comparison with both the Eight Peak Index and the Registry of Mass Spectral Data.

Peak #2:



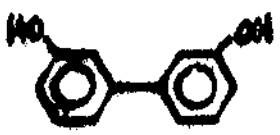
This compound, tentatively identified as **methoxysalicylaldehyde** or **salicylaldehydebenzyl alcohol**, was found only on the alumina surface in Trial I. Identification was made by fragmentation pattern analysis. The molecular weight is 152. The strong fragment at 120 corresponds to loss of the methyl alcohol or methoxy group. The fragment at 91 indicates the loss of the aldehyde function.

Peak #3:



2,4,6-trichlorophenol was identified in Control I and the aqueous phase of both experimental Trials. Identification was clear from comparison with the Eight Peak Index and the Registry of Mass Spectral Data.

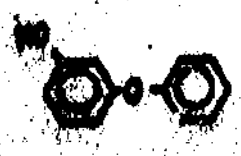
Peak #4:



2,2'-diphenol was identified only on the alumina surface in Trial I. Identification was made by comparison with the Eight Peak Index.

Peak #5: The very small peak of an apparent atomic weight of 220 was present only on the alumina surface in Trial II. The mass spectrum did not yield sufficient information for identification.

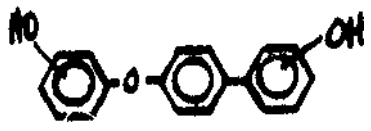
Peak #6:



2-phenoxy phenol was identified in both the aqueous layer and on the alumina surface in Trial I. Identification was by comparison to the Eight Peak Index.

Peak #7: This compound of atomic mass 253 was identified only on the alumina surface in Trial II. The fragment at 213 indicates loss of a carboxylic acid group. The distinctive pattern in the low molecular weight region indicates an aliphatic portion. Together the implication is of a fatty acid.

Peak #8:



Phenol biphenylol ether was tentatively identified in a very large peak in the aqueous phase of Trial I. The fragment at 169 corresponds to the loss of the phenol and ether group. Since the sample was not methylated, it is possible that the oxygen of the alcohol function of the biphenyl portion of the ether is actually positioned as another ether function.

Peak #9:

Trichlorodihydroxy biphenyl was identified on the alumina surface in Trial I and in the aqueous phase in Trial II. Its presence in Trial II may have been as a result of contamination, since the compound was identified in a previous column blank. Following the blank, an attempt was made to "burn off" the contaminant from the column at high temperature. After the "burn off," a "clean" column blank was run prior to proceeding with the Trial II analysis. Identification was by comparison to a spectrum printed in the Doctoral Thesis of Evangelos Voudrias (1984, p.152). The spectrum is virtually identical, displaying a strong parent peak and fragments at M-35 (M-Cl); M-36 (M-HCl); M-63 (M-ClCO); M-70 (M-2Cl); M-71 (M-HCl-Cl); and M-99 (M-HCl-Cl-CO). According to Lotjonen et al (1979), this is the characteristic fragmentation pattern of

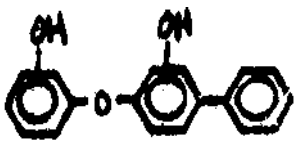
trichlordihydroxybiphenyls. Voudrias notes that "the presence of a very strong (parent peak) M-70 (M-2Cl), however, indicates that at least one -OH group ... is in the 2-position in the ring system." (Voudrias, Ph.D. thesis, 1984, p.153).

Peak #10: Not even a tentative identification was made of this compound of apparent atomic weight 284, although it displayed a clear mass spectrum. It was found only on the alumina surface in Trial II. An aliphatic portion is obvious in the low molecular weight region. Fragments exist at M-43 (possibly $COCH_3$); M-57 (possibly two carbonyl groups and a hydrogen); M-71; M-85; M-99; and M-113. There is a very strong fragment at 129 (M-155).

Peak # 11: Another unidentified compound found only on the alumina surface in Trial II. There is clear indication of an aliphatic portion. Apparent atomic weight is 312. Fragments are at M-56 (two carbonyl groups); 239, indicating subsequent loss of a hydroxyl group; 213; and 185. As with peak #10, a strong fragment appears at 129. The compound may be a fatty acid.

Peak #12: An unidentified compound of atomic weight 278, found only on the alumina surface in Trial I. There appears to be aliphatic portion from the pattern in the low molecular weight region. The fragment at 201 (M-77), along with the very strong fragment at 77 indicate the presence of at least one phenyl group. The fragment at 183, a loss of an additional 18, implies a hydroxyl group. The fragment at 173, 28 less than 201, points toward loss of a carbonyl function.

Peak #13:

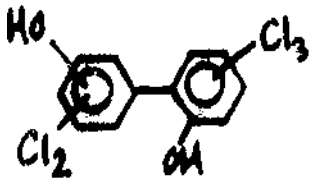


This phenol biphenylel ether, isomeric to peaks #8 and #17, appears to be present in both the aqueous phase and the alumina surface in Trial I, although the parent fragment is obscured in the alumina spectrum. The 260 (M-18) fragment is very strong.

revealing facile loss of water. The 231 fragment shows the loss of a phenyl group. The 168 fragment (M-110), corresponds to loss of the phenol and ether functions.

Peak #14: This compound could not be identified. It shows strong fragments at 168 (M-108) and 139 (M-137) and appears to be monochlorinated by the isotope ratio reflected in the parent fragment.

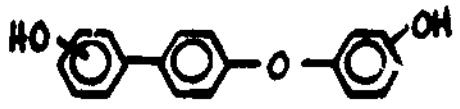
Peak #15:



Pentachorobiphenyldiol was identified on alumina in Trial I. Identification was by extrapolation from spectra of lower chlorinated biphenyldiols published by Lotjonen et al (1979). A "work area spectrum" of the actual mass spectrum was very helpful in emphasizing certain fragments. The fragment at 320 (M-36) corresponds to loss of HCl, indicating, according to Lotjonen, that at least one hydroxyl function is in the ortho-position. Loss of HCl yields the stable dibenzofuran configuration. As expected, a strong fragment exists at 286 (M-70, 2Cl). Loss of an additional 17 (M=269) corresponds to a hydroxyl function. A strong fragment exists at 176 (M-180), corresponding to a loss of all 5 chlorines as HCl. Subsequent loss of another 28 (M=148) reveals a CO function.

Peak #16: This compound, found on alumina in Trial II could not be identified. Apparent atomic weight is 340. There are clear signs of an aliphatic portion from the pattern in the low weight region. There was a rough correspondence to the spectrum found in the EPA/NIH Mass Spectral Data Base of octadecanoic acid butyl ester, $Me(CH_2)_3OC(O)(CH_2)_{16}Me$. Both show characteristic fragments at 340, 285, 241, and 129. The match was not close enough for positive identification, but the unknown compound may be related.

Peak #17:



This compound was tentatively identified as a **phenol biphenylol ether** by interpretation of the sparse fragmentation pattern. If identification is correct, the compound would be isomeric to Peaks #8 and #13. The fragment at 168 (M-110) corresponds to loss of the phenol and ether functions. The fragment at 139, an additional loss of 29, could result from the subsequent loss of COH. The 128 fragment (M-150) could be the biphenyl after a loss of its hydroxyl function. The fragment at 77 indicates at least one phenyl group.

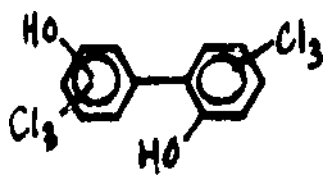
Peak #18: No identification was made of this rather noisy spectrum from alumina surface in Trial I. The apparent molecular weight is 334. The 319 fragment (M-15) points to a methyl group. The fragment of 278 (M-56) could be the loss of two carbonyls. The strong peak at M=77 indicates the presence of at least one phenyl which easily fragments from the rest of the compound.

Peak #19: The spectrum did not provide sufficient information for identification. An aliphatic portion is apparent and the molecular weight appears to be 278.

Peak #20: The mass spectrum reveals substantial information, but no identification could be made. The small fragment at 318 (M+2) implies that there may be a chlorine. There are strong fragments at M-45 (COOH) and M-80 (COOH, Cl). The fragment at 168 could be a biphenyl ether or biphenylol. The fragment at 202 may indicate that the Cl is attached to the biphenylol. The 139 fragment is the loss of another 29, a COH function.

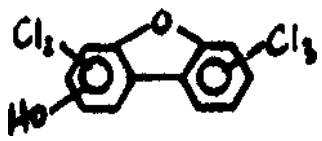
Peak #21: The fragmentation pattern yields information insufficient for identification.

Peak #22:



Hexachlorobiphenyldiol was identified on alumina in Trial I. The spectrum reveals a typical polychlorinated biphenyldiol fragmentation pattern as described by Lotjonen et al (1979). The isotope distribution fragmentation pattern is typical of hexachlorinated species. The initial loss of 36 (HCl) indicates that at least one hydroxyl is in the 2-position (Lotjonen, 1979), yielding a stable dibenzofuran configuration. The M-64 fragment is also typical, according to Lotjonen, corresponding to ClCO. M-70, 320, is the loss of 2 Cl. 291 shows the subsequent loss of a carbonyl, followed by another chlorine at 256, a carbonyl at 228 and another HCl at 192.

Peak # 23:

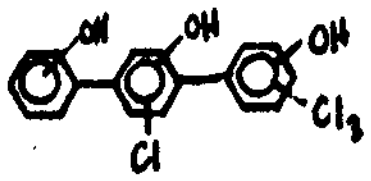


Pentachlorodibenzofuranol was identified on alumina in Trial I by fragmentation pattern interpretation. Strong fragments exist at 319 (M-35, Cl); 291 (CO); 255 (HCl); 226 (COH); and 191 (Cl). The fragment at 160 could be the dibenzofuran minus the chlorines and hydroxyl group.

Peak #24:

Hexachlorodibenzofuran was identified in Trial I by its fragmentation pattern. The parent peak shows the isotope ratio typical of a hexachlorinated compound. There are strong fragments at 309 (M-63, ClCO); 274 (Cl); 239 (Cl); 204 (Cl); and 169 (Cl). The 187 fragment shows a loss of OH from the fragment at 204.

Peak #25:

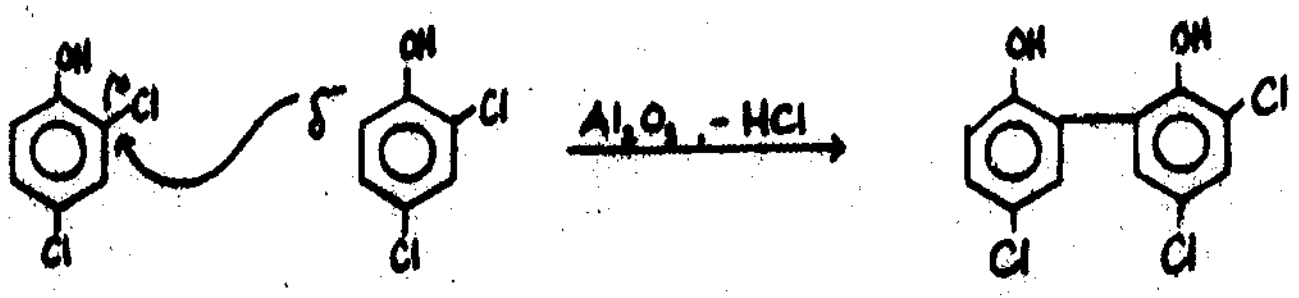


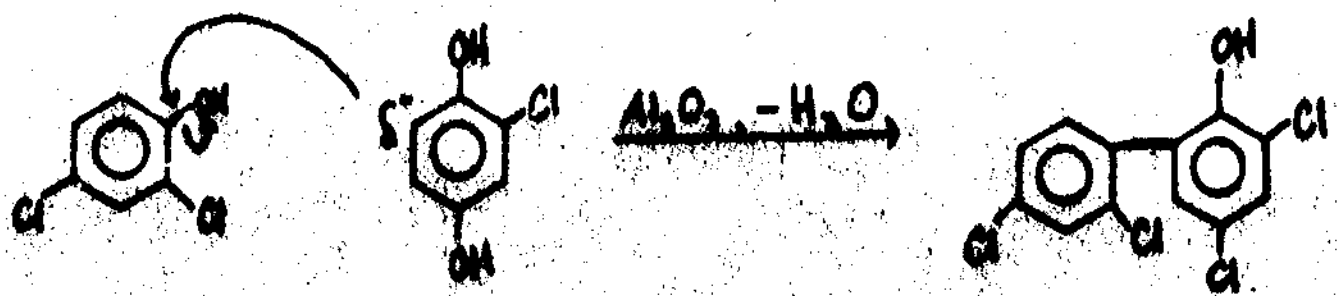
Tetrachlorotriphenol was identified by fragmentation pattern interpretation in Trial I alumina and Trial II aqueous phase. The parent shows a tetrachlorinated isotope ratio. Small fragments appear at 380 and 343 which could indicate lost chlorines. The largest fragment is at 218 (M-196) which corresponds to the loss of the trichlorophenol group. The fragment at 126 corresponds to the chlorophenol, and 91 roughly corresponds to the phenol. The trichorophenol appears, minus its hydroxyl and one chlorine, at 143. The M-63 fragment could be ClCO.

V.D. Reaction Mechanisms

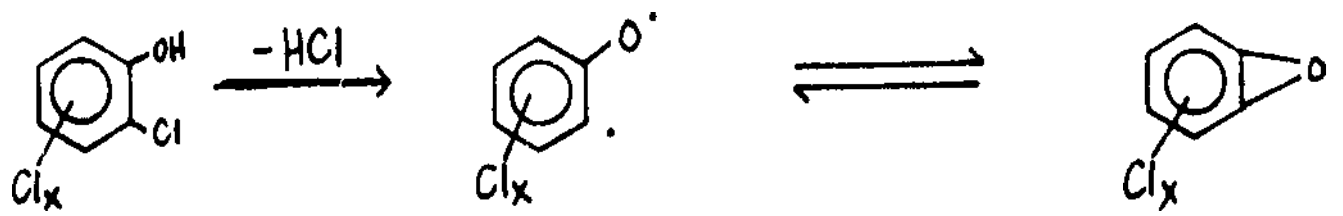
V.D.1. Biphenyl Formation

Many of the observed reaction products formed in the free chlorine, dichlorophenol reaction in the presence of aluminum oxide have reacted to form biphenyl groups. The reaction can proceed as described in Section III.A.6.b., "Intermolecular Substitution by Nucleophilic Carbon Atoms." Many examples are given of substitutions to substituted ring compounds in which alcohol, or another ortho-, para-directing group has activated the ortho- and para-carbons to be nucleophilic. A biphenyl may be formed similarly from chlorophenols:

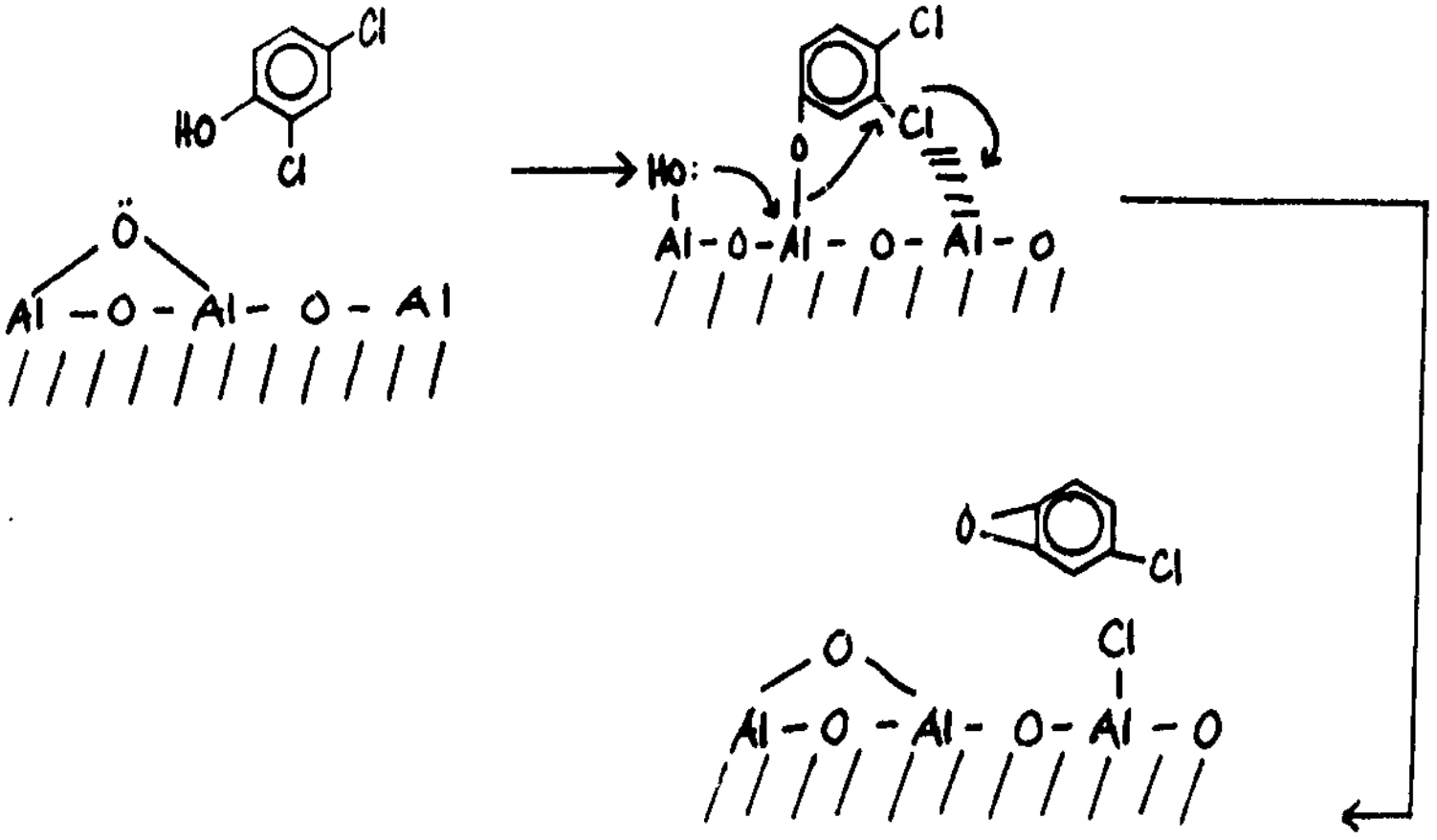




Zoller and Ballschmiter (1986) suggest an intermediate in the formation of chlorinated dibenzofurans from chlorophenols and chlorophenates which may also provide a route to biphenyls.



The alumina surface may facilitate formation of this intermediate, thus making possible its formation at lower temperatures than the 320-440°C observed by Zoller and Ballschmiter. Strained Al-O-Al bridges are known to cleave O-H bonds, leaving a phenoxy group coordinated to the alumina surface (Posner, 1978). Exposed aluminum atoms are acidic and can accept the lost chlorine (Posner, 1978).

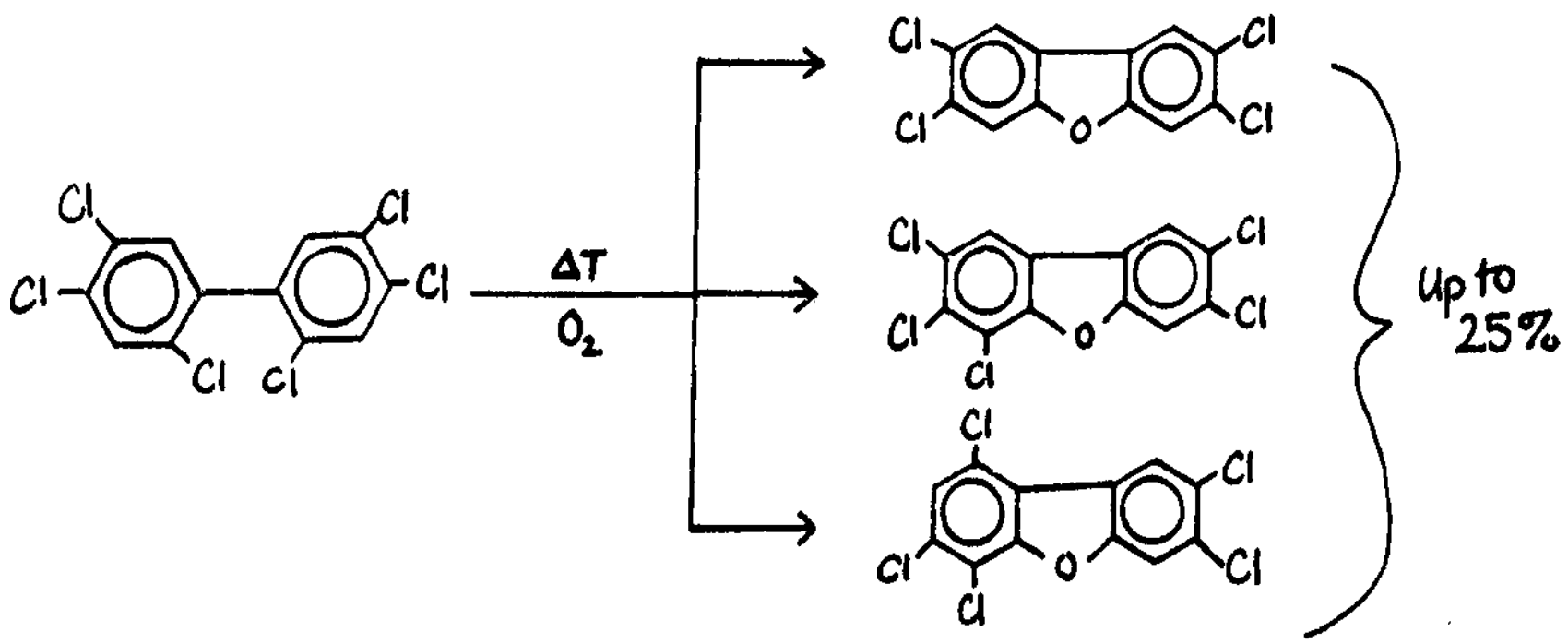


The epoxide intermediate provides an excellent site for attack by the nucleophilic ortho-carbon of a chlorophenol.

This mechanism also explains the positioning of a hydroxyl group in the 2-position in several of the reaction products observed.

V.D.2. Polychlorinated Dibenzofuran Formation

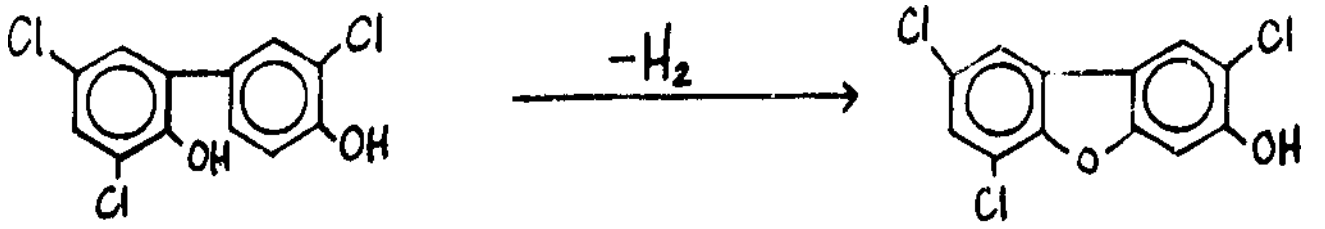
It is well documented that polychlorodibenzofurans (PCDF's) and polychlorodibenzo-p-dioxins (PCDD's) can result from heating polychlorinated biphenyls (PCB's) (Hryhorczuk et al, 1986; Stephens, 1986; Schecter, 1986). Building fires in which PCB's are present often provide reaction conditions sufficient for oxidizing the PCB's to PCDF's or PCDD's. Rappe et al (1979) provide the following scheme for the pyrolytic formation of PCDD and PCDF from PCB's:



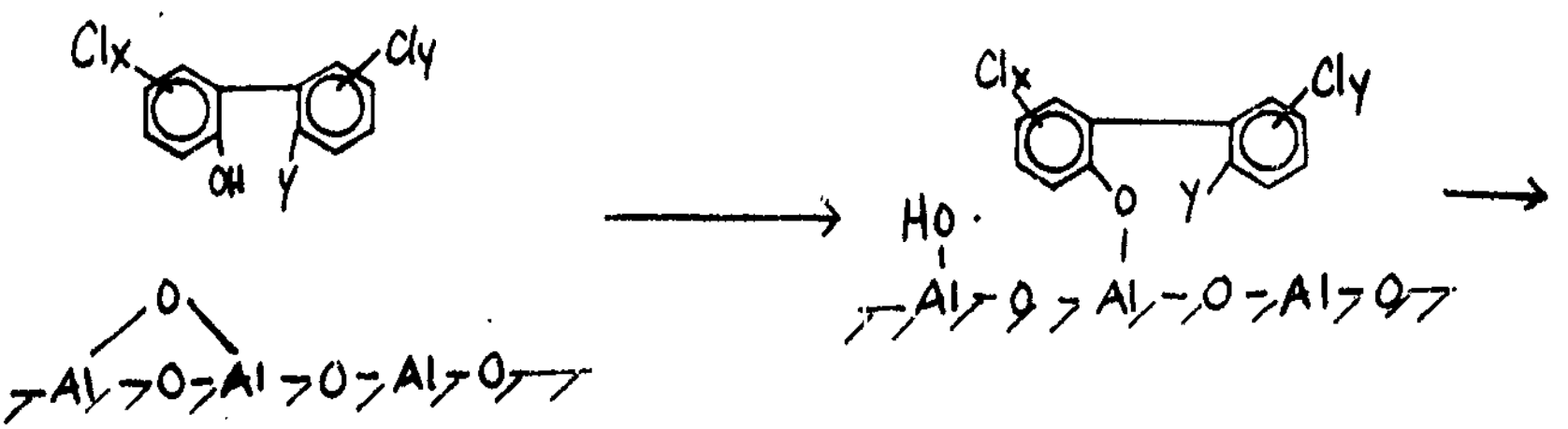
Polychlorodibenzofurans are known to be formed also from PCB's when exposed to ultraviolet light, (Buser and Bosshardt, 1977; Kimbrough, 1974).

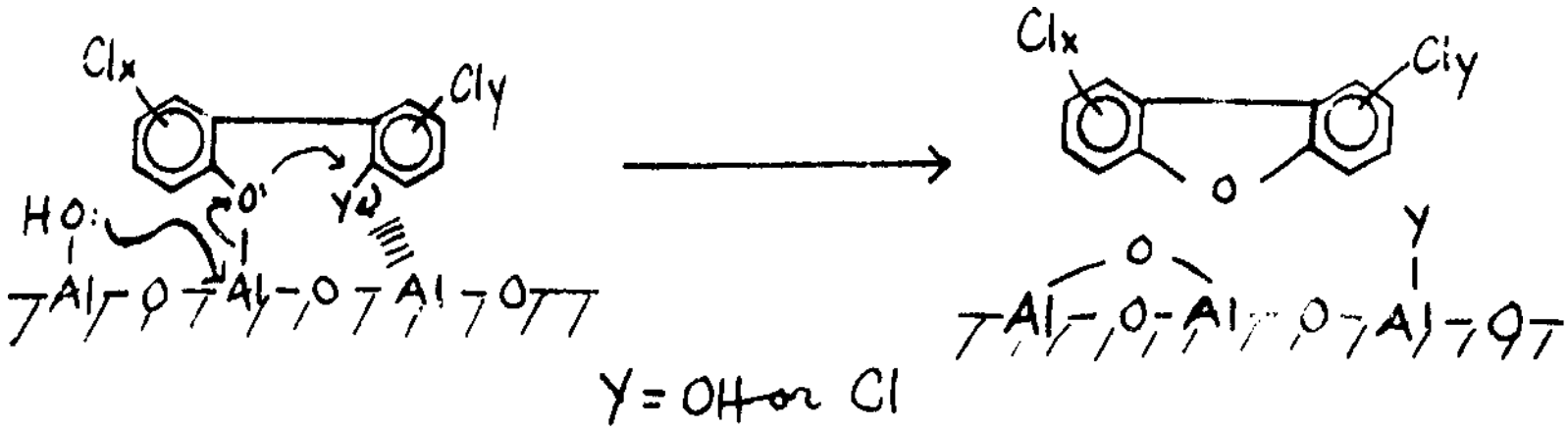
PCB $\xrightarrow[O_2]{UV}$ PCDF 2% yield

Since the polychlorinated biphenyls identified in this experiment were hydroxylated, they provide an even more facile route to PCDF's.

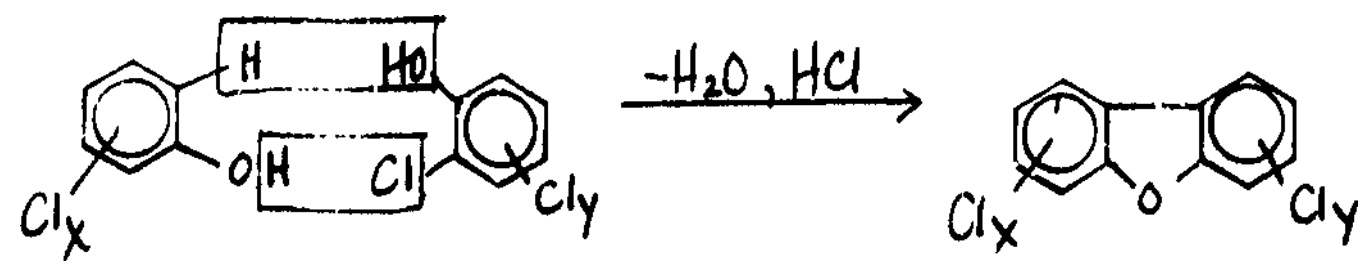


Posner's reaction mechanism scheme emphasizes how the alumina surface could facilitate this reaction. He states, "Active alumina, having some strained Al-O-Al rings, is known from spectroscopic studies to cleave the heteroatom-H bonds of alcohols ... with attachment of the resultant alkoxide to the alumina surface. Because most of the reactions reported here proceed under such mild conditions, it seems reasonable to invoke also activation of the reactant by coordination of its heteroatom 'Y' to one of the acidic aluminum atoms exposed on the alumina surface." (Posner, 1978)





The formation of PCDF's directly from chlorophenols (not via PCB's as above) is also well documented. Zoller and Ballschmiter (1986) propose the following route:

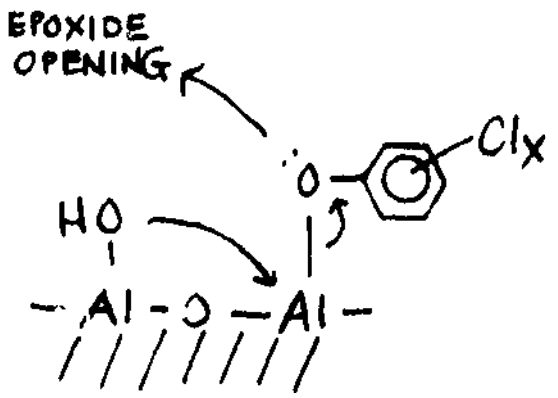


They report this reaction occurring at temperatures between 320-440°C with a reaction time of from 3-15 hours.

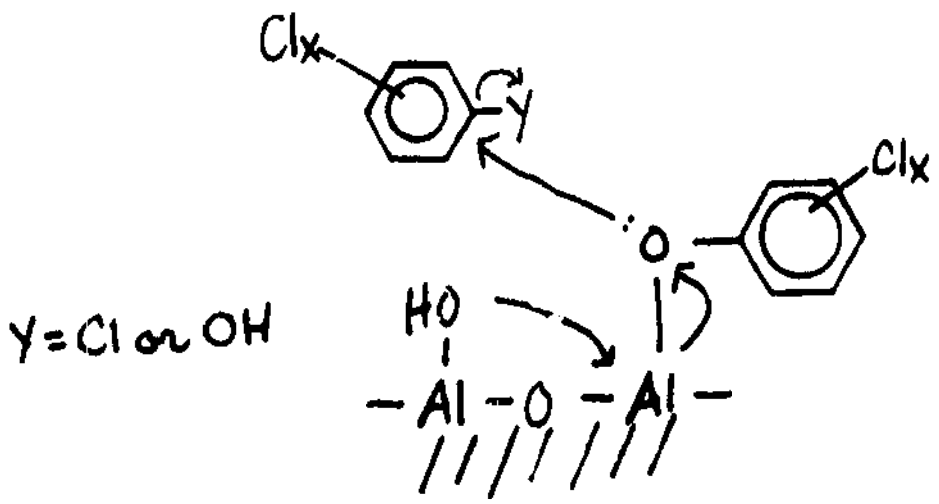
The alumina surface must have facilitated the reaction in order for it to have occurred at the room temperature conditions observed. Several examples of alumina-facilitated dehydrations are shown in the literature review section III.A.7.a., "Elimination of H-OH from Alcohols." The loss of HCl may proceed as shown in the above mechanism for PCDF formation from PCB's.

V.D.3. Ether Formation

Many identified compounds have a phenoxy phenol function. The ether linkage could be made quite readily via the epoxide proposed by Zoller and Ballschmiter (1986) and shown in section V.D.1., "Biphenyl Formation." The reaction would be similar to several presented in section III.A.4.a., "Intermolecular Addition of OH and Other Heteroatom-H Groups." The OH bond could be cleaved by the alumina surface as presented in the biphenyl formation mechanism, with the alumina stabilizing the phenoxy intermediate.



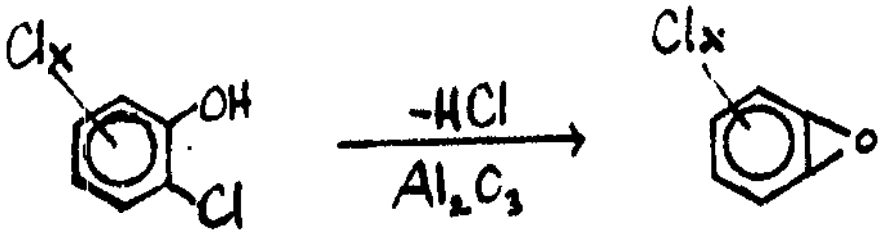
This same phenoxy could displace a chlorine or hydroxyl group of another chlorophenol molecule in an intermolecular substitution reaction.



The reaction would be facilitated even further if the heteroatom, "Y" group were coordinated to an acidic aluminum atom exposed on the catalyst surface.

V.D.4. <u>Dechlorinations</u>

Many of the identified products have undergone dechlorination from their original dichlorophenol groups. Zoller and Ballschmiter (1986) note that the epoxide intermediate they propose for PCDF formation from chlorophenols results in loss of a chlorine.



The ether, biphenyl, and dibenzofuran formation reactions proposed above can result in loss of chlorine. The loss is facilitated by the exposed, acidic aluminum atoms which accept the chlorine leaving group.

Several dehalogenations are cited in section III.A.7.e., "Elimination of Halogens," which occur mostly under harsh conditions (>300°C). However, the dehalogenation cited in section III.A.7.e. by Jigajinni et al involves two dehalogenations, one of which occurs at 50°C, the other at 120°C.

V.D.5. Chlorinations

Room temperature chlorination reactions occurred even in the uncatalyzed Control I.

$$\text{2,4-dichlorophenol} \xrightarrow[\text{no alumina}]{Ca(OCl)_2} \text{2,4,6-trichlorophenol}$$

It is unnecessary to posit an alumina-catalyzed chlorination mechanism.

VI. THE JAVITS LECTURE CENTER FIRE

On September 26, 1986, a fire broke out in a storage room in the Jacob Javits Lecture Center at the State University of New York at Stony Brook. Substantial concentrations of the highly toxic polychlorodibenzo-p-dioxins (PCDD's) and dibenzofurans (PCDF's) were released, which adhered to soot which was distributed widely in the building via the hallways and air ventilation system. Classes were held in the building as soon as two to three hours after the fire was extinguished, although students, faculty, and staff complained of extreme discomfort. Classes were held in even the worst effected portions of the building until almost one month after the fire. It was more than one week after the fire before any substantial clean-up effort took place, and visible soot deposits remained on walls and ceilings of the building for as long as eight months. The Lecture Center was closed only after two full semesters of classes had gone on in the building.

An independent panel of experts selected by a University task force subsequently recommended comprehensive testing and clean-up by a company experienced in hazardous waste removal. A health survey of students, faculty, and staff who used the Center was also recommended.

Twenty cases of vinyl floor buffing pads were consumed in the fire, along with several polyvinylchloride floor tiles and garbage bags. A large drum of "Ajax" cleanser, several plastic chairs, a quaternary ammonium chloride cleaning solution known as "A-33," a wood and plastic desk and several other plastic materials also melted or suffered significant fire damage. The floor buffing pads were coated with a phenol/formaldehyde resin and contained aluminum oxide as an abrasive.

Analysis of soot which was drawn into the air ventilation system of the building during or after the fire revealed the presence of a wide variety of polyaromatic compounds, including PCDD's, PCDF's and polychlorinated biphenyls (PCB's). Results of tests conducted by Zenon Testing laboratories of Burlington, Ontario, Canada and Illinois Institute of Technology Research Institute of Chicago of soot taken from various locations in the air ventilation system are shown below. All results are given in parts per billion.

TOXIC CHEMICALS IDENTIFIED BY ZENON TESTING LABORATORIES*

Chemical Name	Sample Number** 1	2
tetrachlorodibenzo-p-dioxin (TCDD)	<1 ppb	<1.5 ppb
pentachlorodibenzo-p-dioxin (P5CDD)	<10	<2
hexachlorodibenzo-p-dioxin (HexCDD)	280	40
heptachlorodibenzo-p-dioxin (HeptCDD)	2300	300
octachlorodibenzo-p-dioxin (OCDD)	3600	720
tetrachlorodibenzofuran (TCDF)	170	5.7
pentachorodibenzofuran (P5CDF)	49	<4
hexachlorodibenzofuran (HexCDF)	<50	<6
heptachlorodibenzofuran (HeptCDF)	270	<10
octachlorodibenzofuran (OCDF)	86	3.7

TOXIC CHEMICALS IDENTIFIED BY IITRI

Chemical Name	Sample Number** 1	2
TCDD	<0.1	0.3
2 3,7,8-TCDD	<0.1	<0.1
P5CDD	1.4	4.8
2,3,7,8-P5CDD	NT***	1.3
HexCDD	44	75
2,3,7,8-HexCDD	NT	23
HeptCDD	339	330
2,3,7,8-HeptCDD	NT	394
OCDD	3250	5890
TCDF	52	139
2,3,7,8-TCDF	2.8	7.1
P5CDF	7.6	11.2
2,3,7,8-P5CDF	NT	4.8
HexCDF	4.3	19.6
2,3,7,8-HexCDF	NT	2.4
HeptCDF	26	34.8
2,3,7,8-HeptCDF	NT	15.2
OCDF	22	36

* Other toxic substances identified include: PCB's (Zenon); pentachlorophenol (Zenon); Benzo[a]pyrene (Zenon); 2-methyl phenol (Zenon); 3-methyl phenol (Zenon); 4-methyl phenol (Zenon); dimethyl phenol (Zenon); asbestos (NY Testing Laboratories); formaldehyde (SUNY at Stony Brook Dept. of Env. Health and Safety); phenol (SUNY at Stony Brook Dept. of Env. Health and Safety)

** Sample #1 was collected from dust which lined the air ventilation intake ducts near the room of the fire. Sample #2 was composed of similar dust taken from ductwork extending as far as the central core of the air ventilation system.

*** No effort was made to determine the percentage of this specific isomer. Only homologue group concentrations were calculated.

Formation of PCDD's and PCDF's during high temperature combustion is the subject of intense international research due largely to the release of these extremely toxic compounds from mass-burn municipal solid waste incinerators.

It is widely held that lignin provides the aromatic groups necessary for the basic three ring structure of PCDD's and PCDF's (Griffin, 1986). These can be chlorinated by various sources of free chlorine, notably polyvinyl chloride plastics from which chlorine is easily liberated by heat (Balischmiter, et al, 1986).

Domalski et al (1986) combusted a simulated municipal solid waste composed of cellulose, sand and polyvinyl chloride under controlled conditions. Several chlorinated aromatic compounds were formed, including chlorinated benzenes, chlorinated phenols, and PCB's, but no detectable levels of PCDD's or PCDF's were discovered.

The fire in the Javits Lecture Center liberated substantial quantities of PCDD's and PCDF's. It seems likely that the aluminum oxide present at the fire scene acted as a catalyst, facilitating the formation of PCDD's and PCDF's from phenol and free chlorine. If this was the case, the phenol most likely followed reaction pathways similar to those posited for the products identified in the aqueous phase reaction of chlorophenol, $Ca(OCl)_2$ and alumina. The alumina catalyst would have greatly facilitated the multi-order gas phase reaction, providing both a surface on which the reaction could proceed and catalytic properties described in the preceeding thesis.

VII. SUMMARY AND CONCLUSIONS

Free chlorine reacts with dichlorophenol in aqueous room temperature solution to yield a mixture of the starting product and trichlorophenol. In the presence of aluminum oxide, many additional products are formed, including toxicologically significant compounds such as polychlorodibenzofurans and hydroxylated PCB's. The alumina is observed in the reaction promoting di- and trimerizations, ether formations, dechlorinations, oxidations, substitutions, and epoxide openings.

Review of the literature on alumina catalysis reveals reaction mechanisms which help to explain how the alumina can facilitate reactions that would not usually occur under such mild conditions. Alumina's ability to act simultaneously as an acid and a base is central to its catalytic effect. The surface is able to stabilize reaction intermediates and leaving groups, initiate reactions as an acid or base, and orient molecules favorably for reaction.

Alumina's catalytic properties may be toxicologically significant if people are exposed to certain of the reaction products studied. Some of the proposed uses for alumina in water treatment may result in substantial concentrations of phenols, chlorophenols and free chlorine coming in contact with the alumina surface, thereby creating reaction conditions similar to those studied in the experimental reactions of this paper.

The Javits Lecture Center fire at the State University of New York at Stony Brook provided an example of what may happen when phenol and free chlorine come in contact with alumina at elevated temperatures in the gas phase. The fire released a wide array of chlorinated dibenzo-p-dioxins and dibenzofurans as well as other polyaromatic hydrocarbons which were distributed widely in the building, contaminating many areas, including the air ventilation system.

A better understanding of aluminum oxide catalysis may help to avoid similar potentially hazardous situations in the future.

APPENDIX:
MASS SPECTRA

FIGURE 8: peak 1

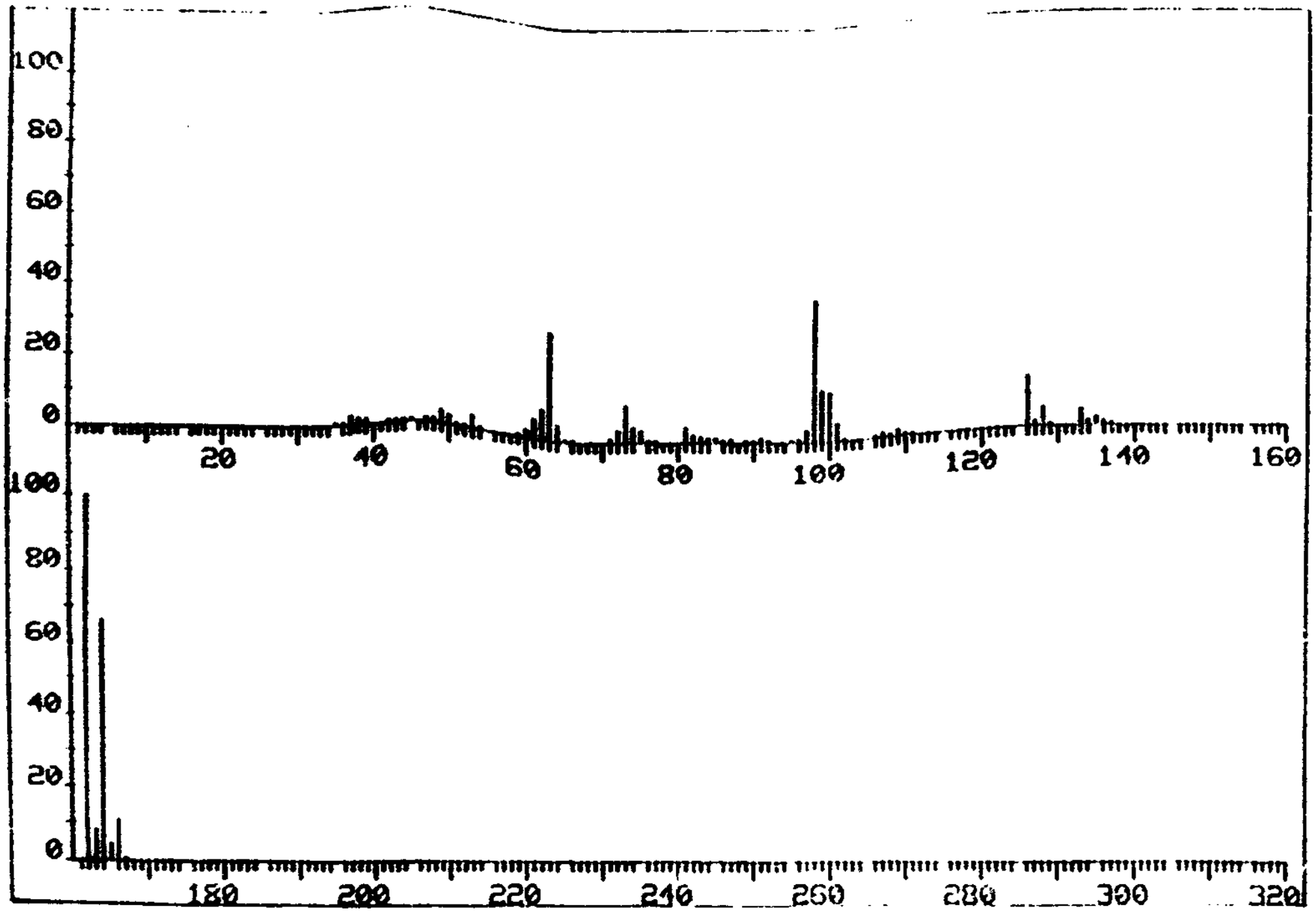


FIGURE 9: peak 2

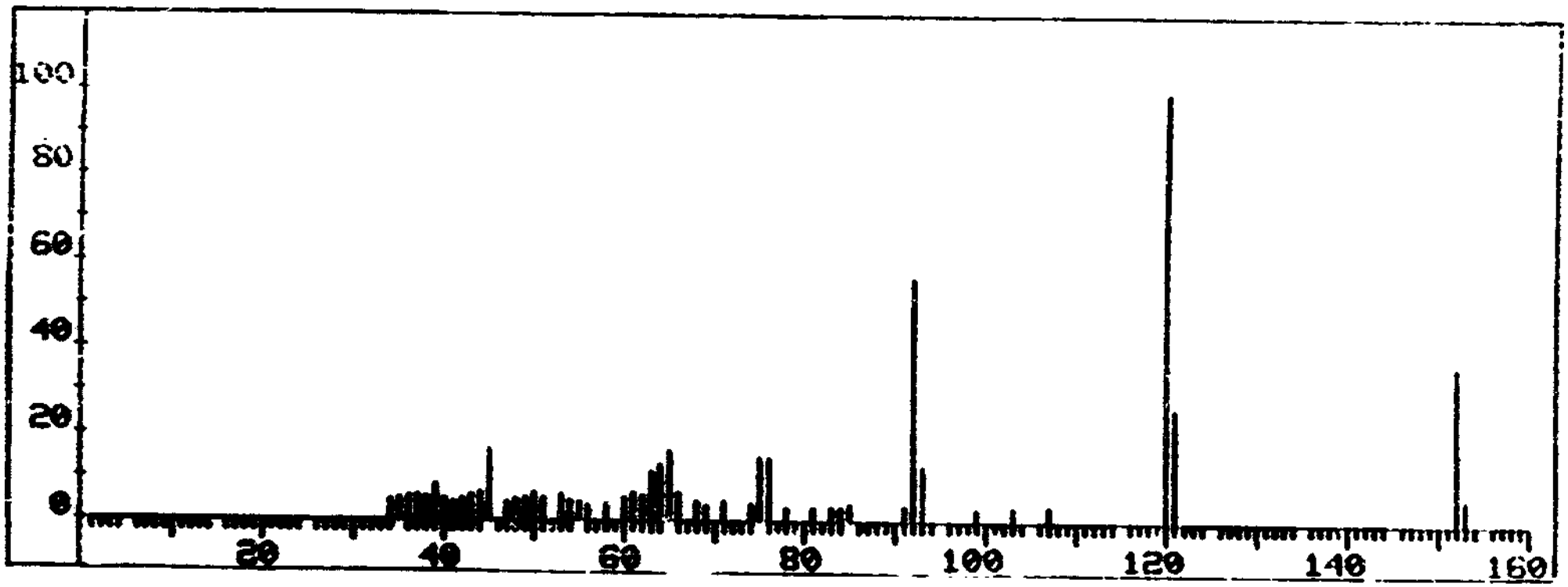


FIGURE 10: peak 3

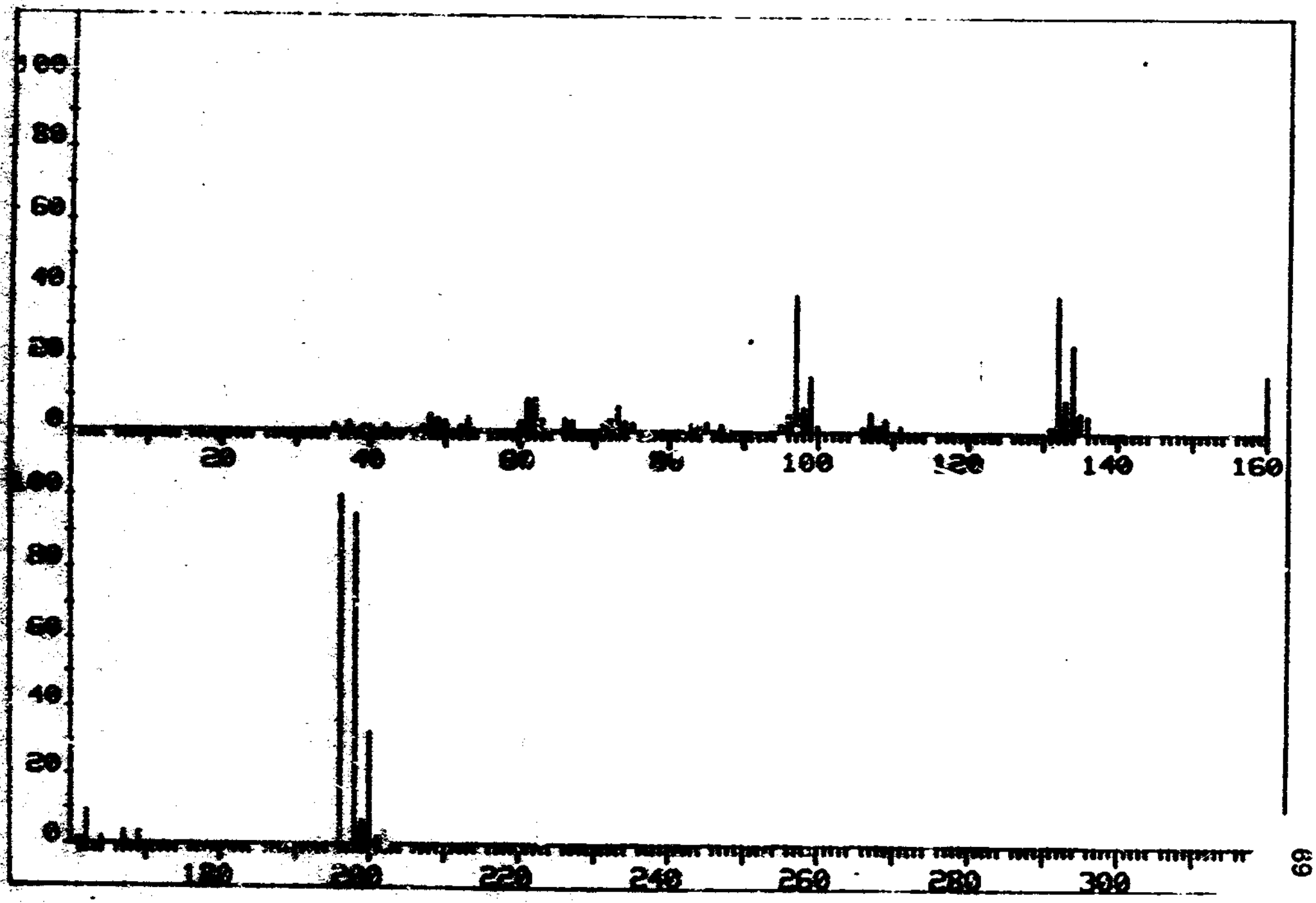


FIGURE 11: peak 4

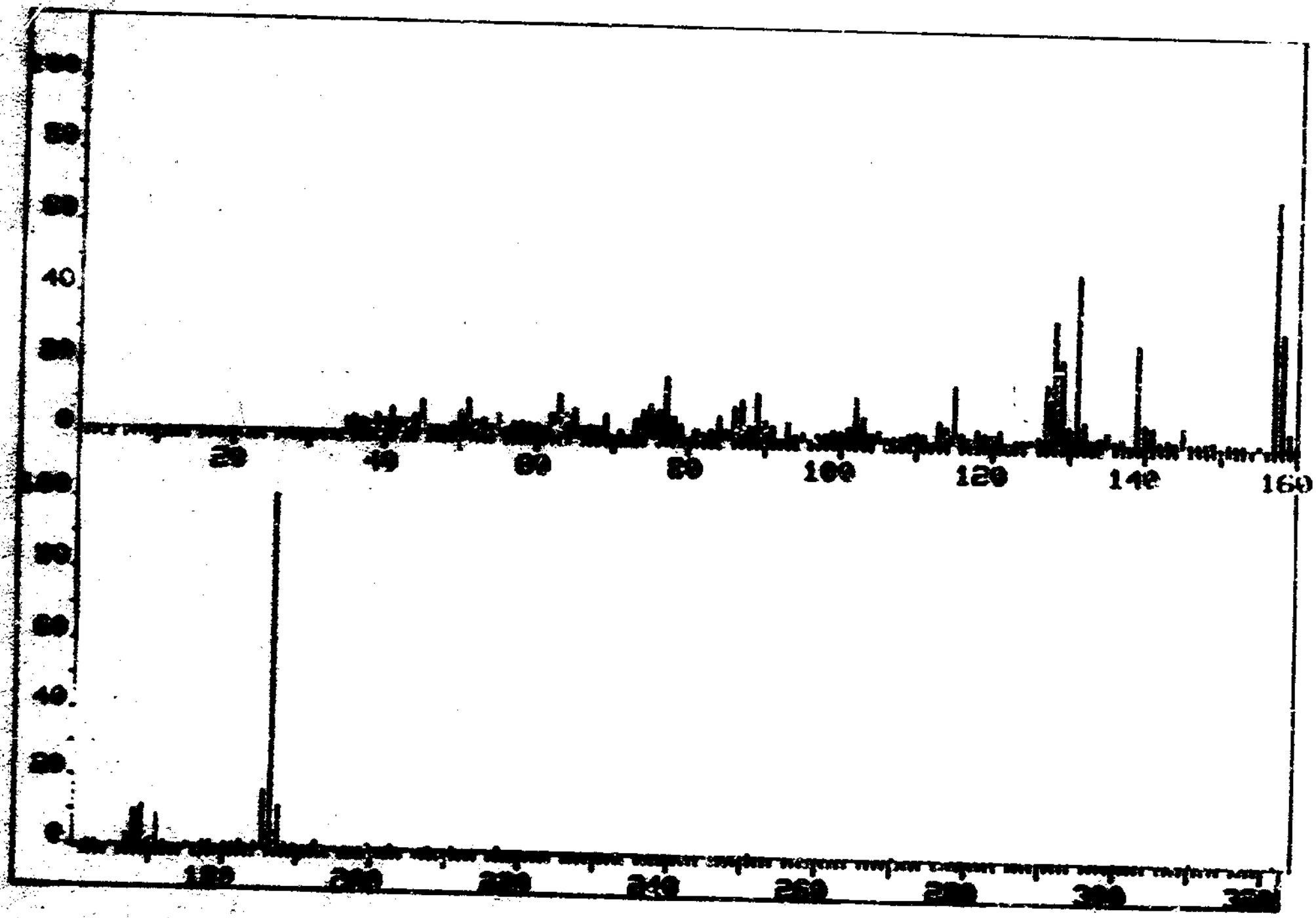


FIGURE 12: peak 5

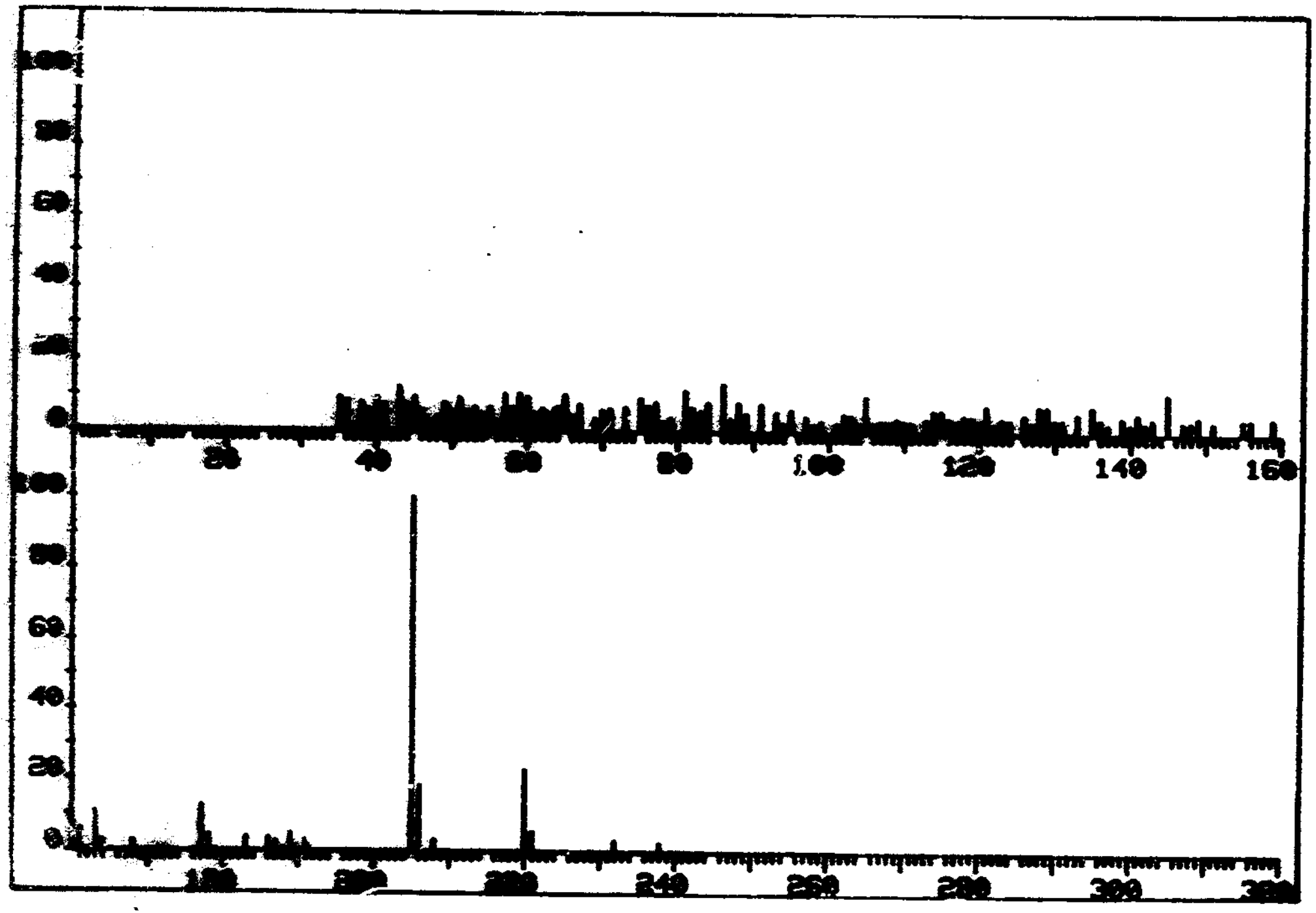


FIGURE 13: peak 6

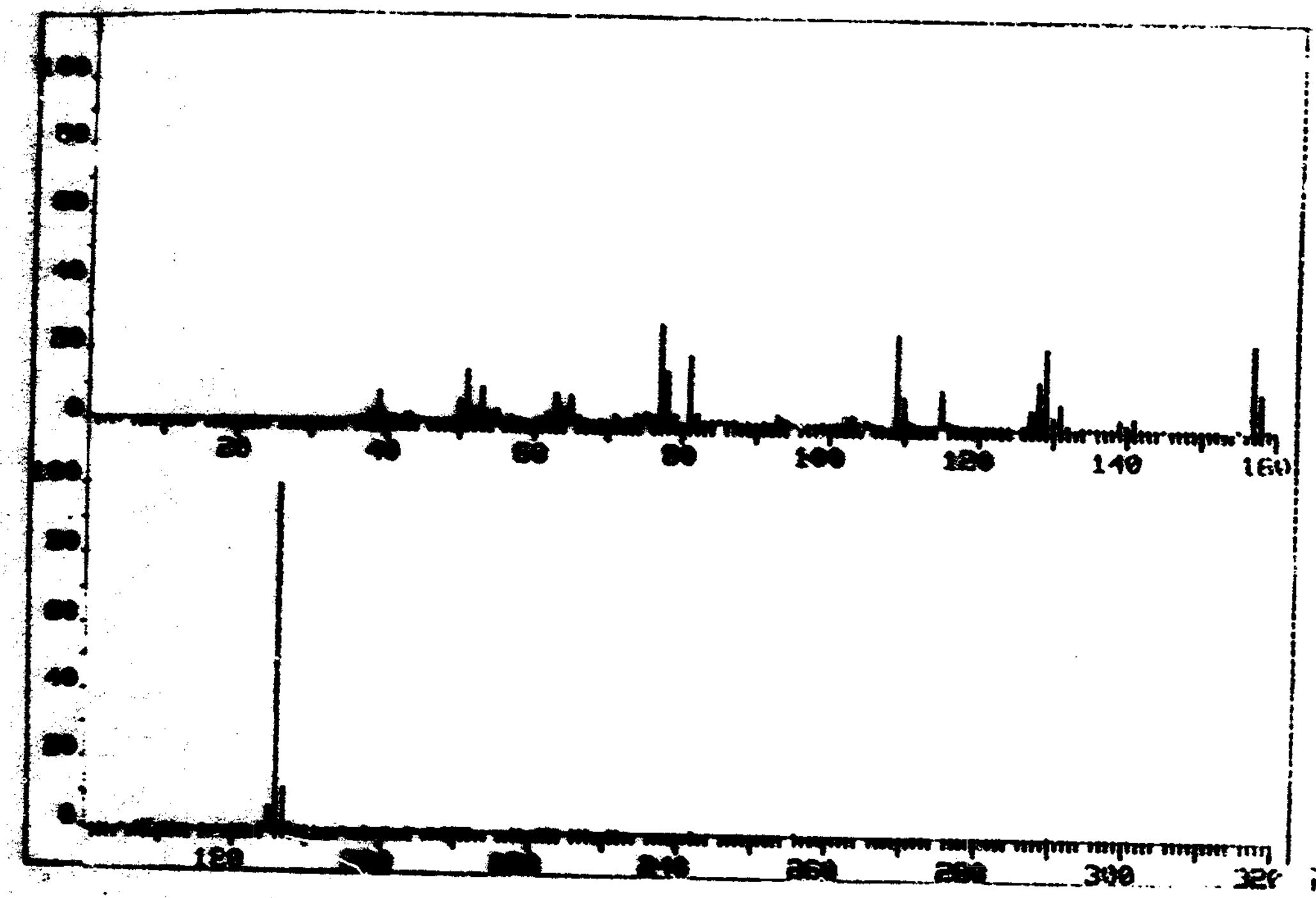


FIGURE 14: peak 7

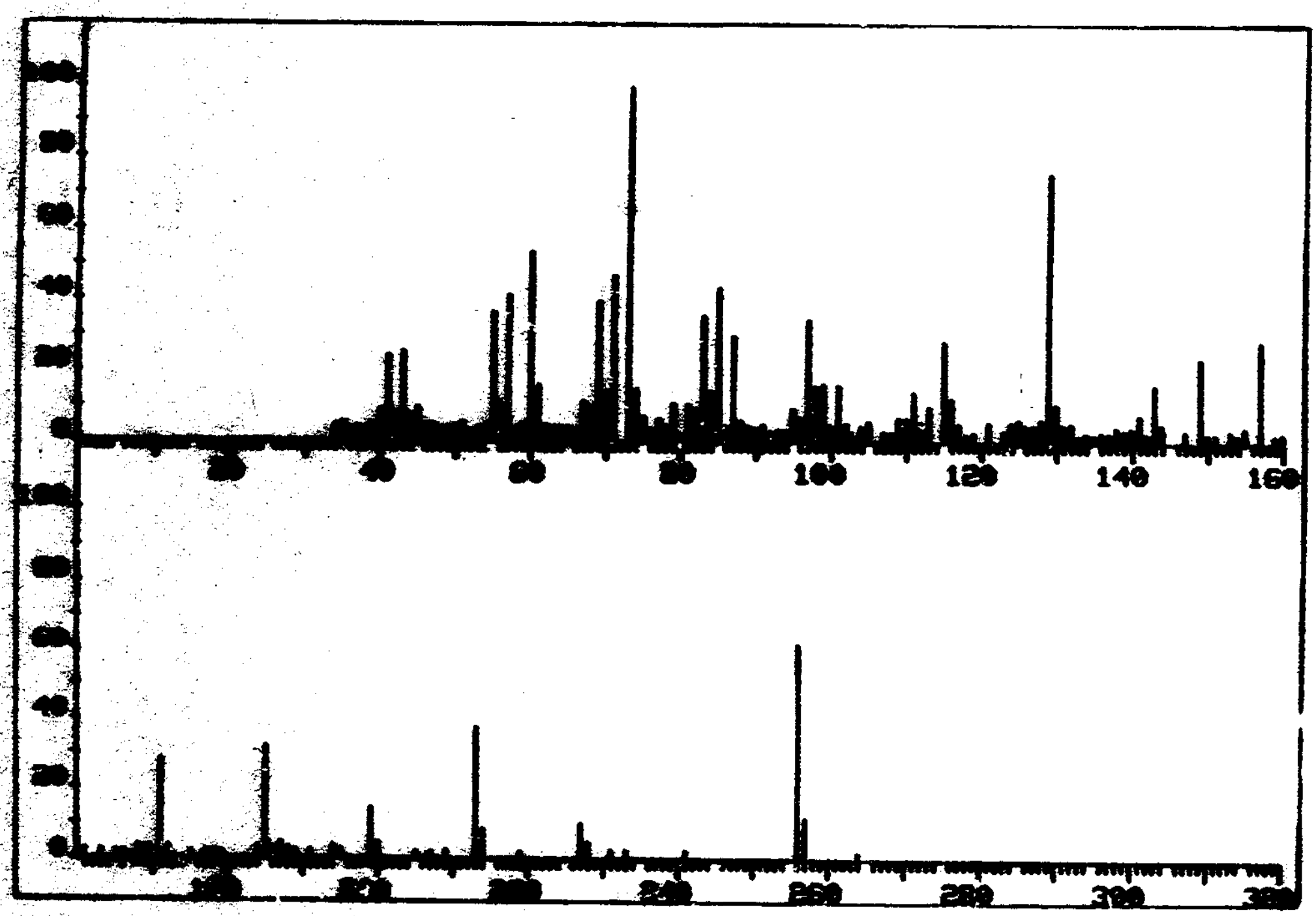


FIGURE 15: week 8

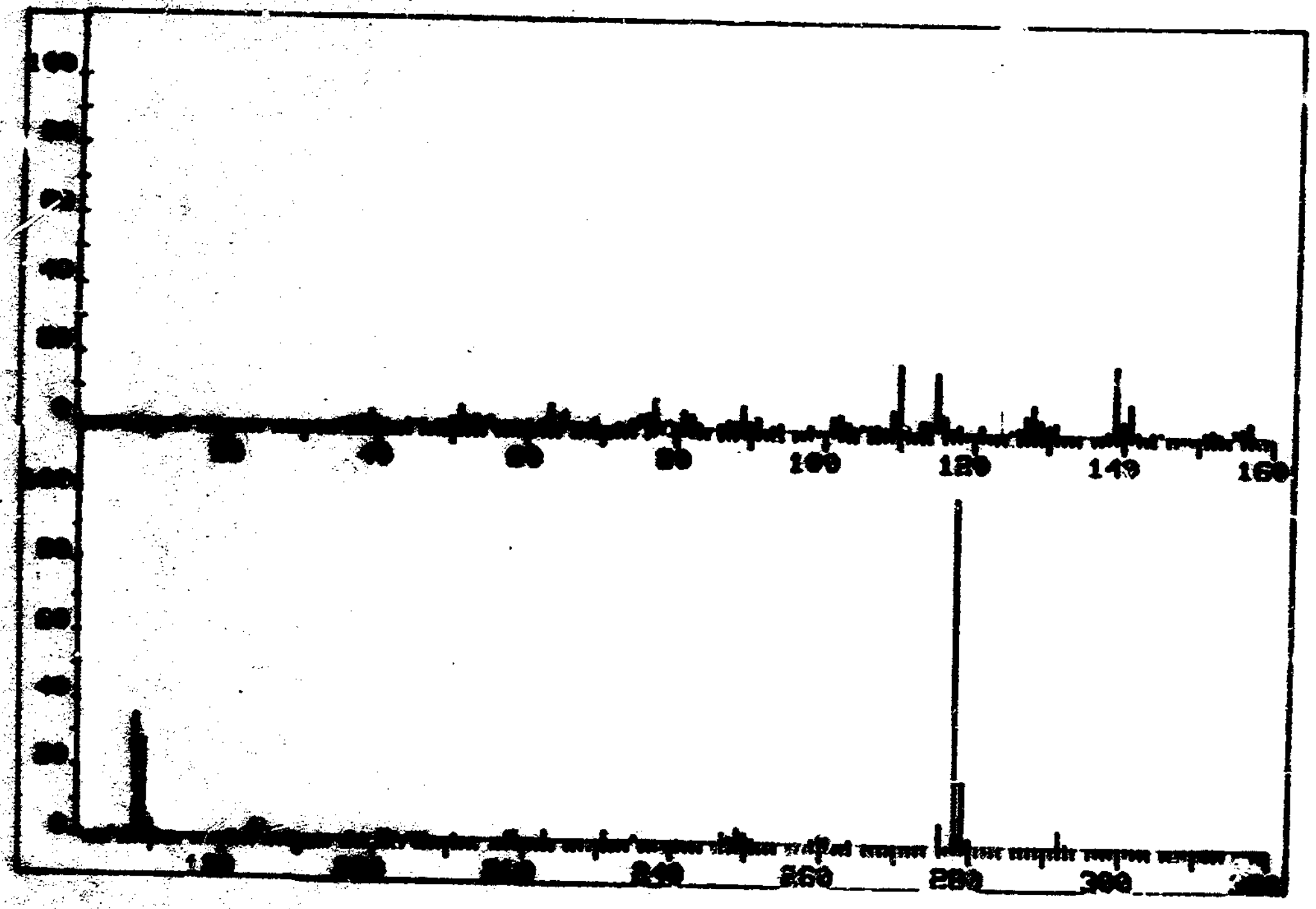


FIGURE 16: peak 2

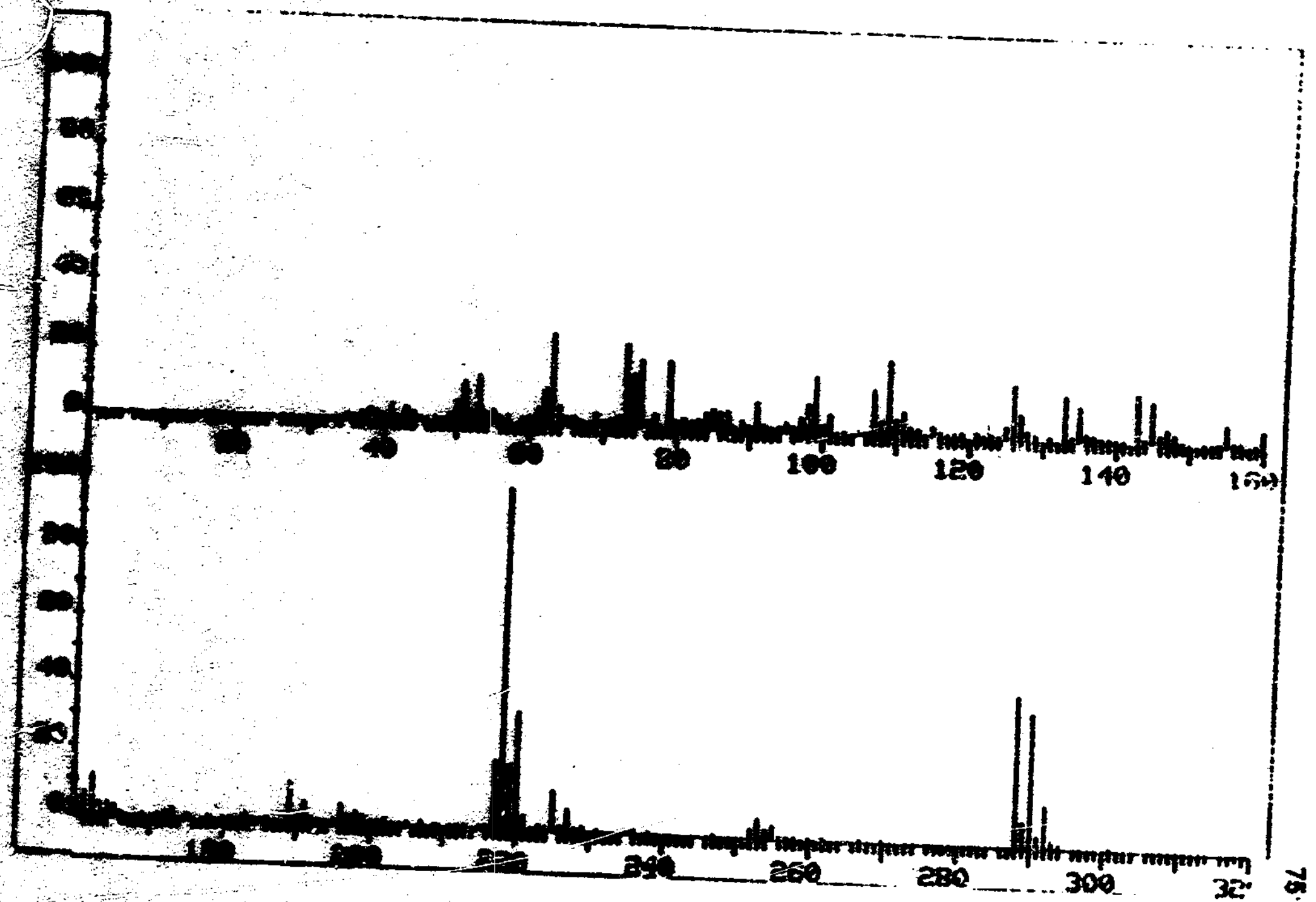


FIGURE 17: peak 10

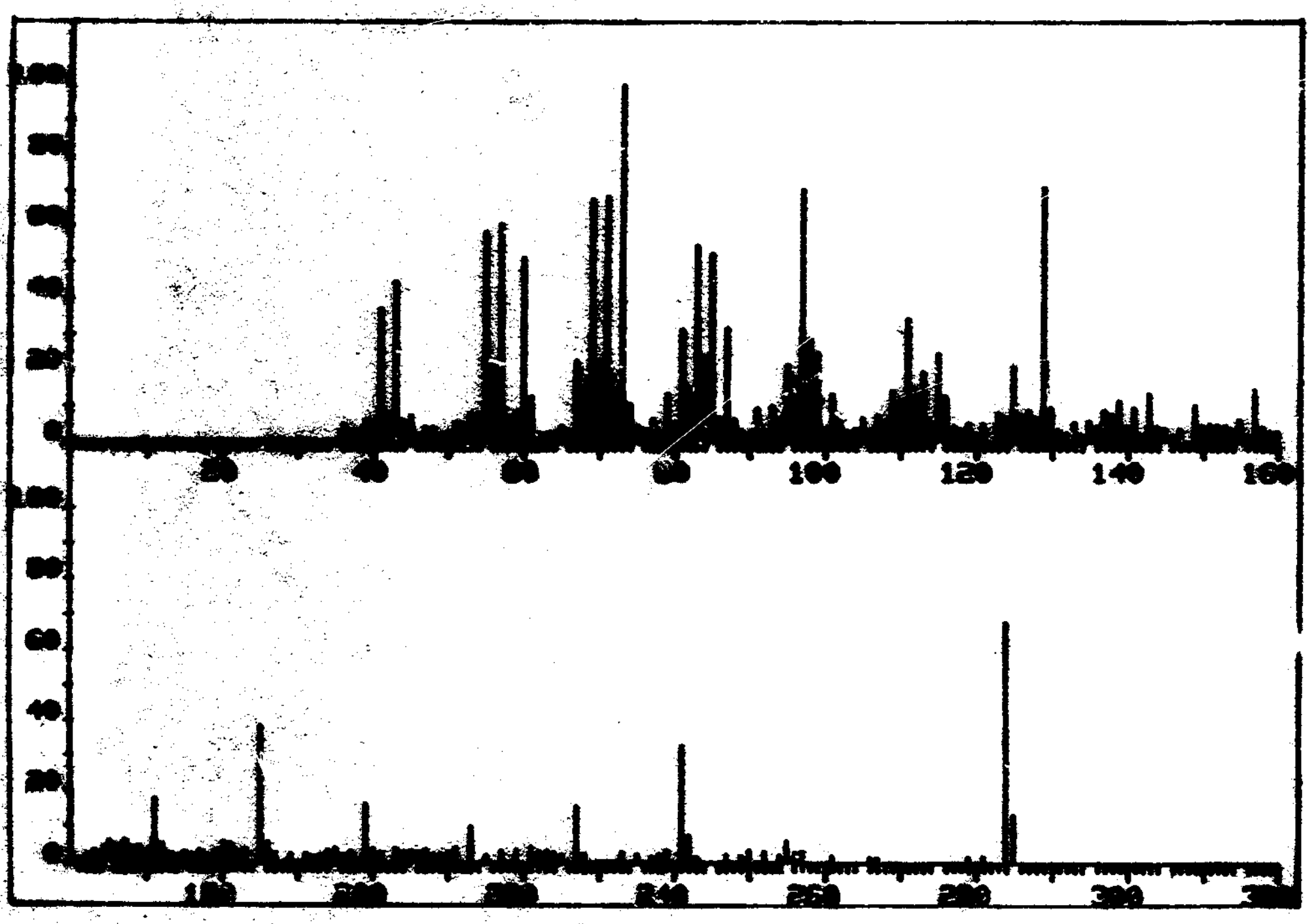


FIGURE 13: peak 11

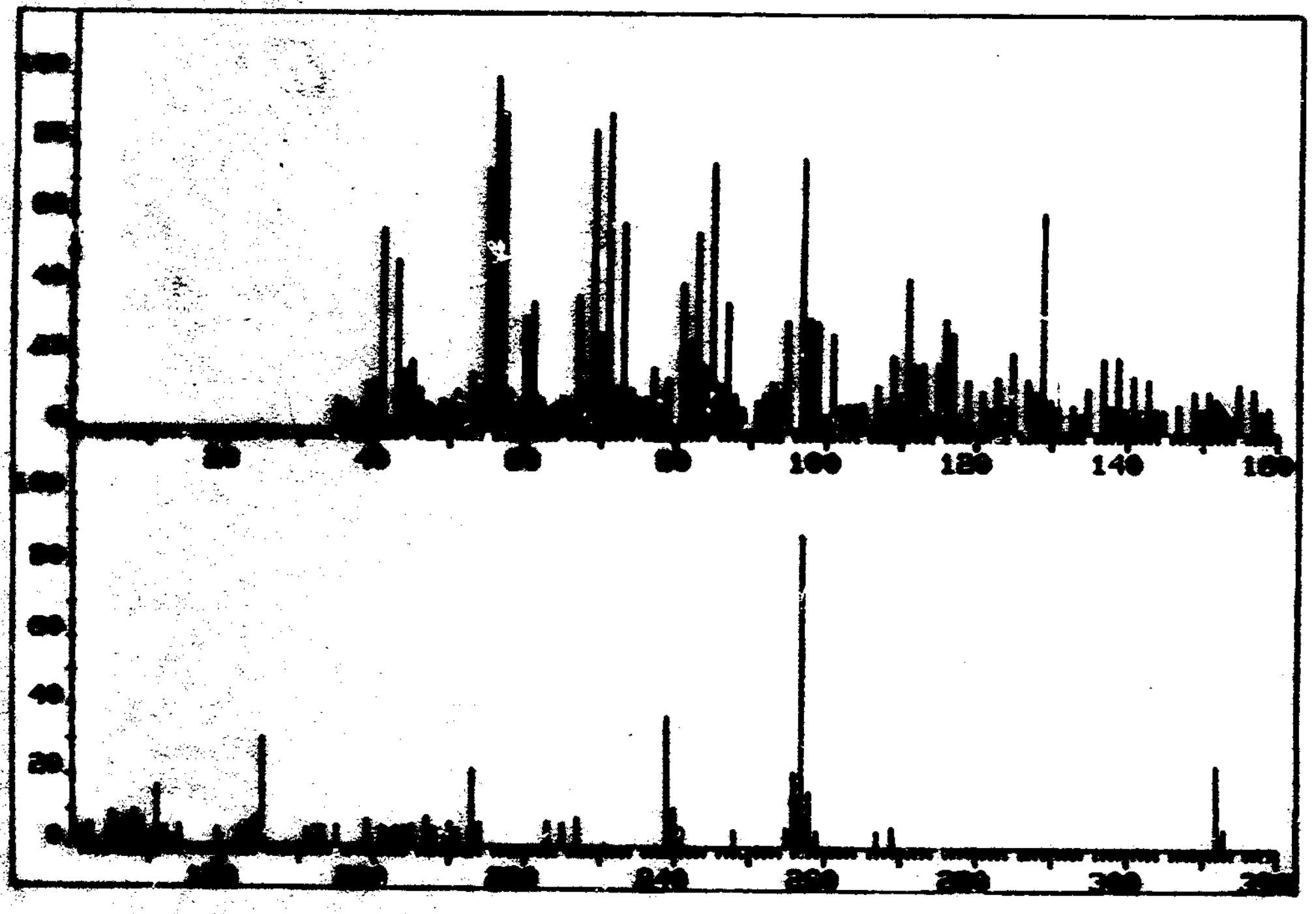


FIGURE 19: peak 12

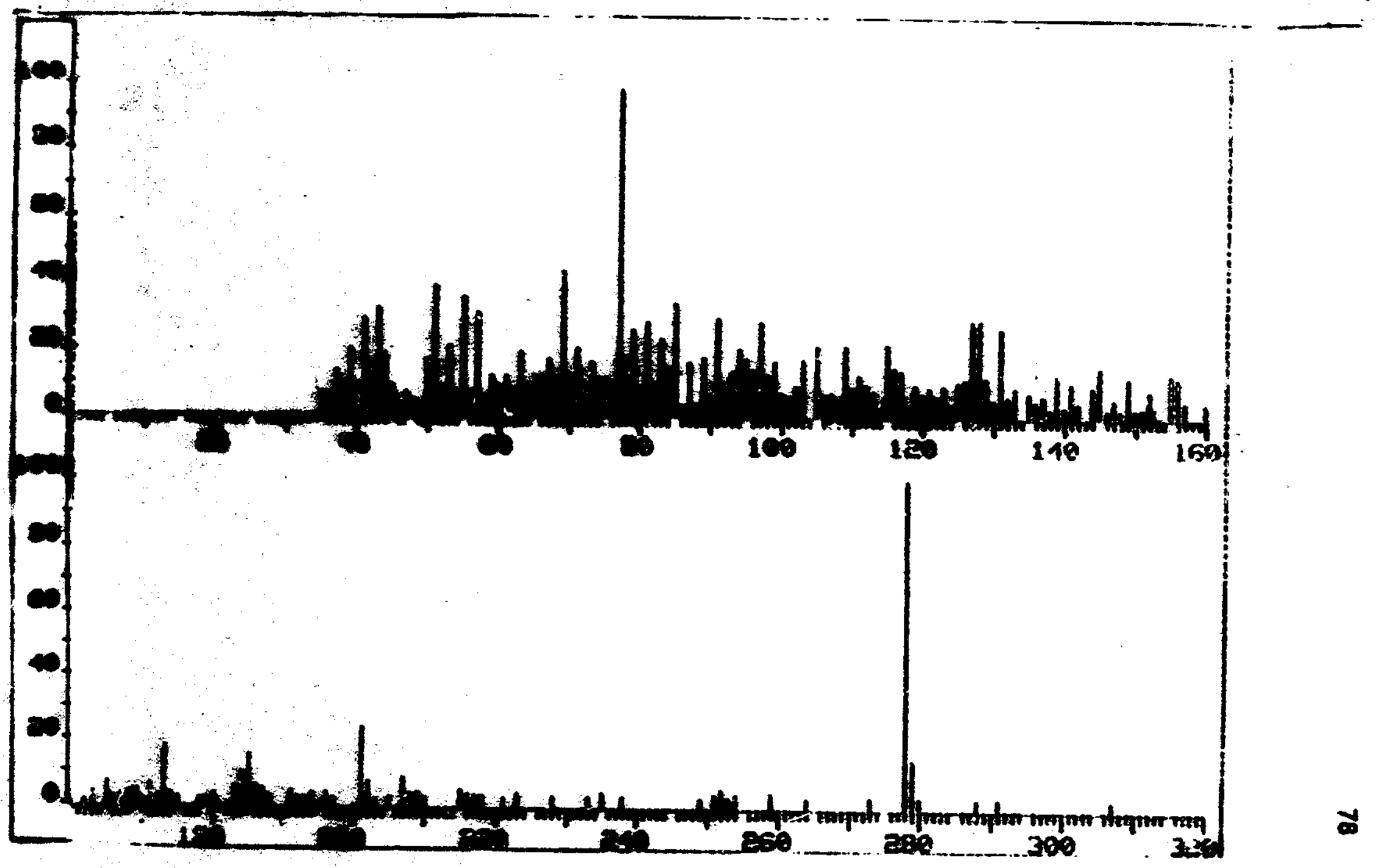


FIGURE 20: Peak 13

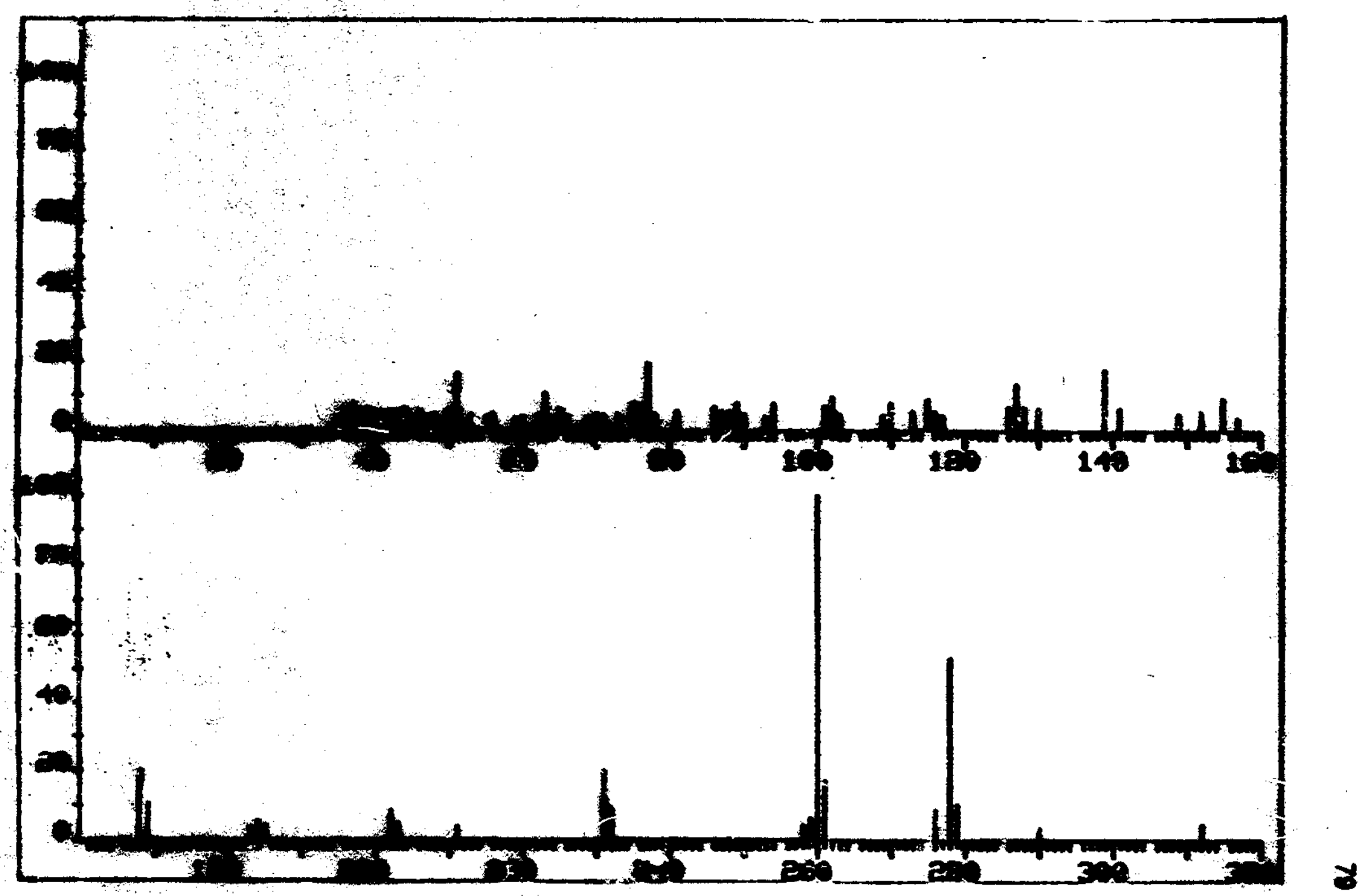


FIGURE 21: peck 14

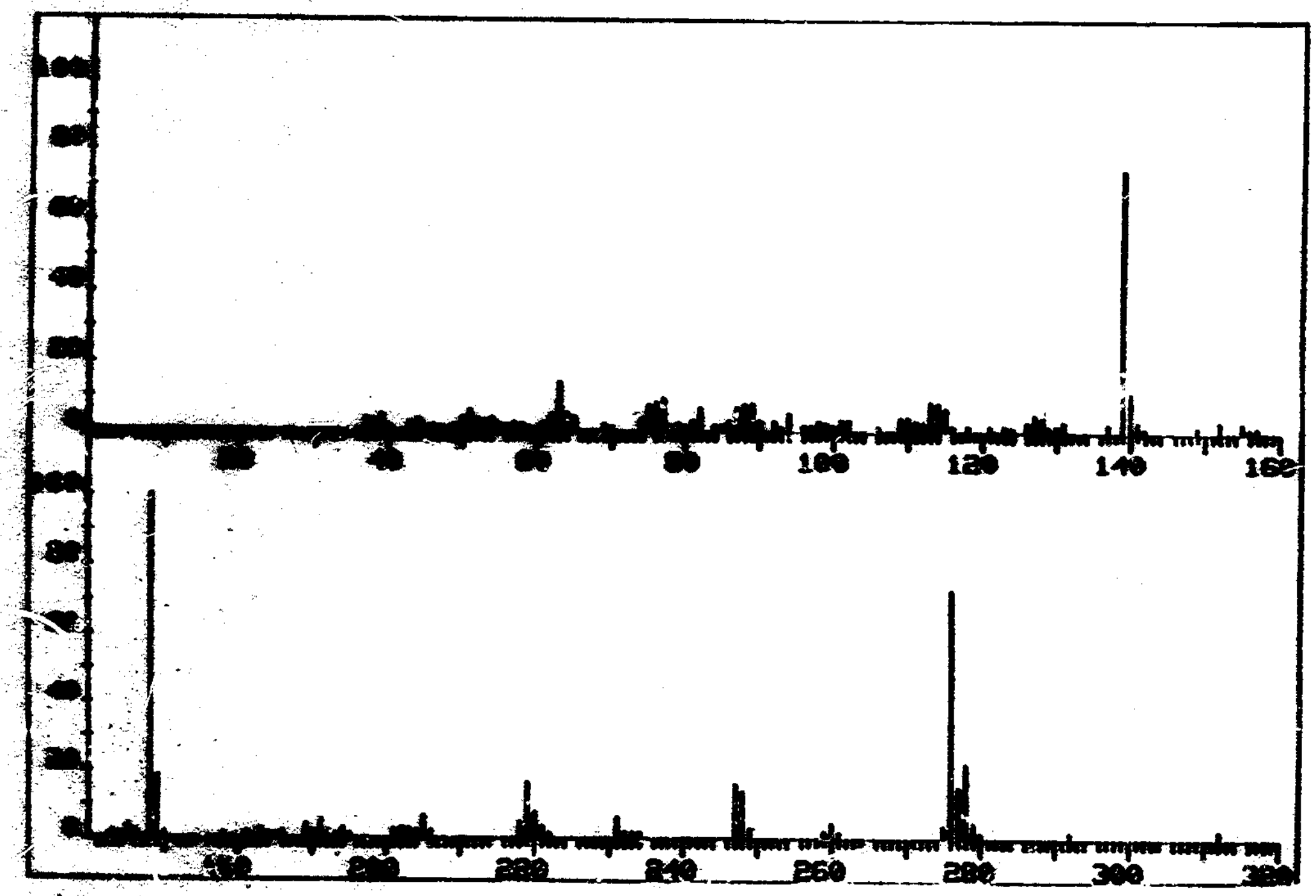


FIGURE 22: peak 15

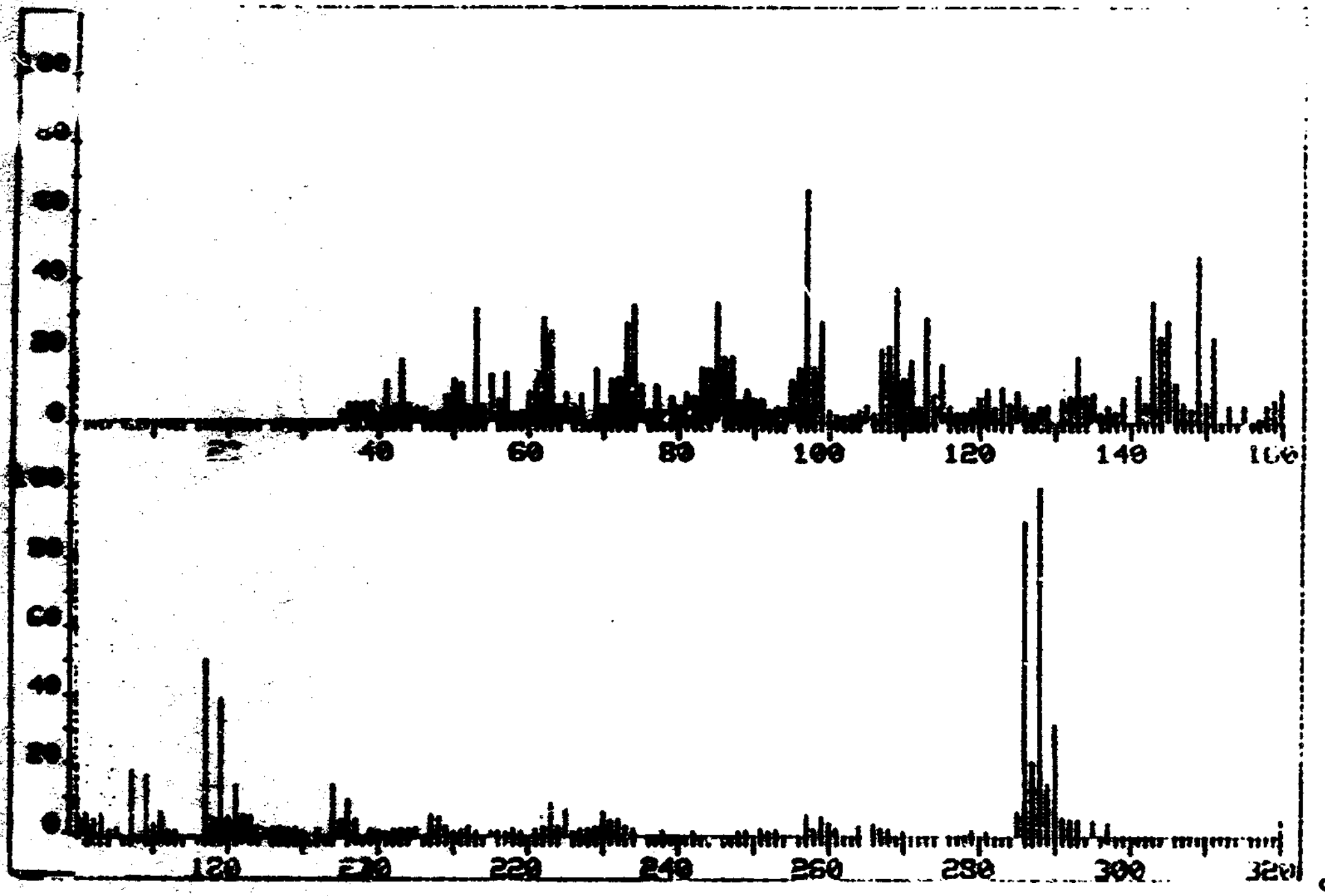


FIGURE 22a: peak 15 work area

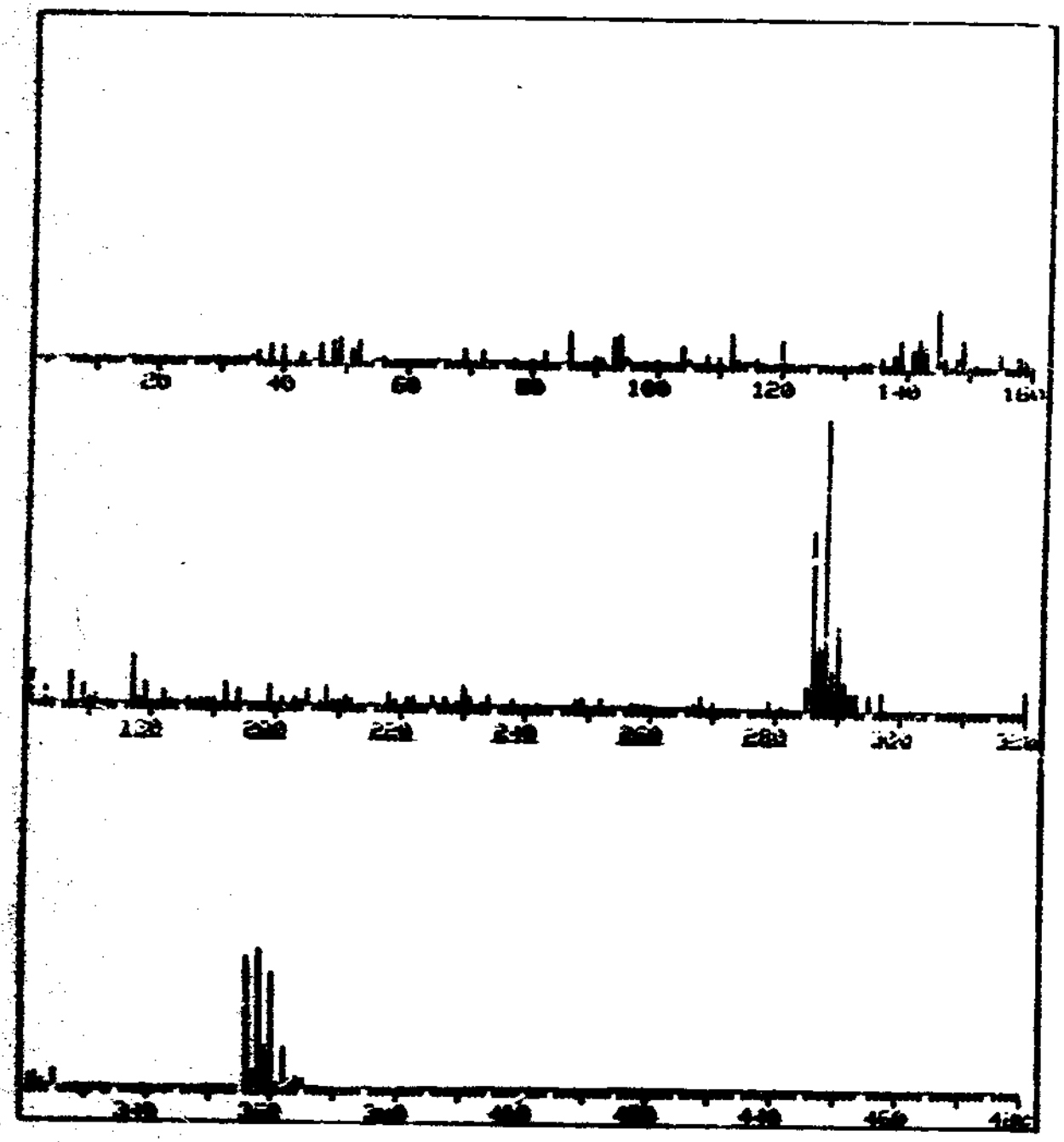


FIGURE 23: peak 16

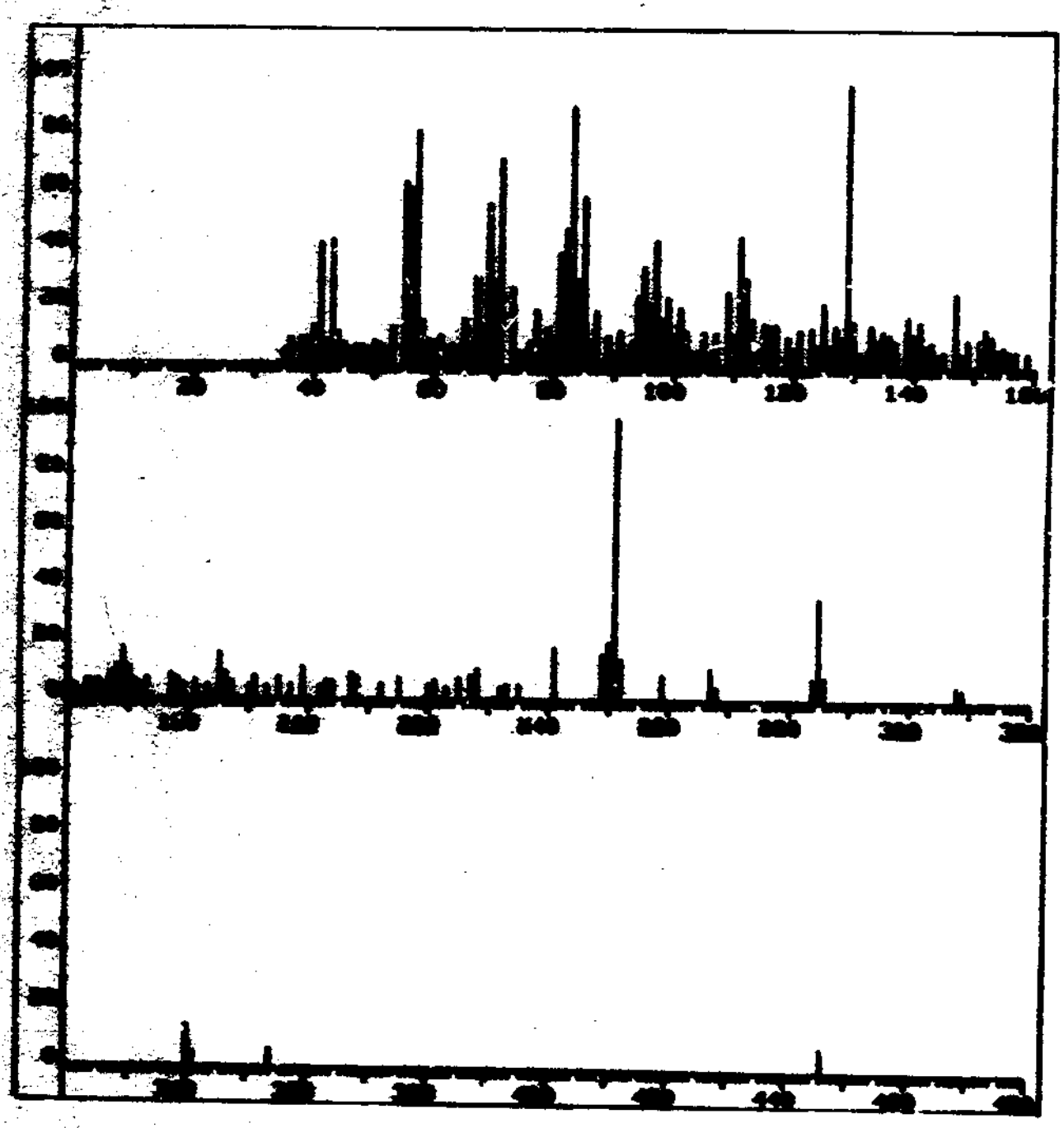


FIGURE 24: peak 17

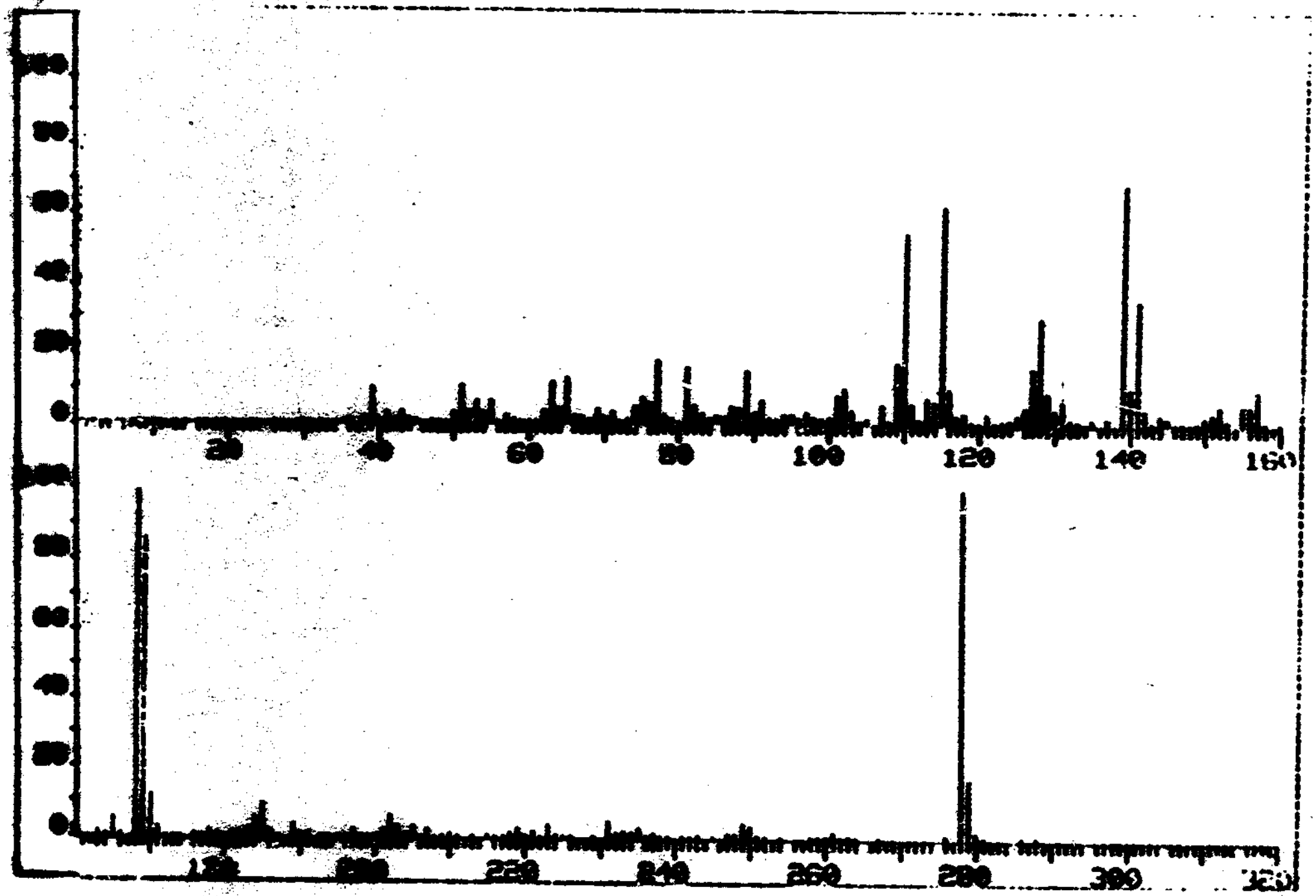


FIGURE 25: peak 18

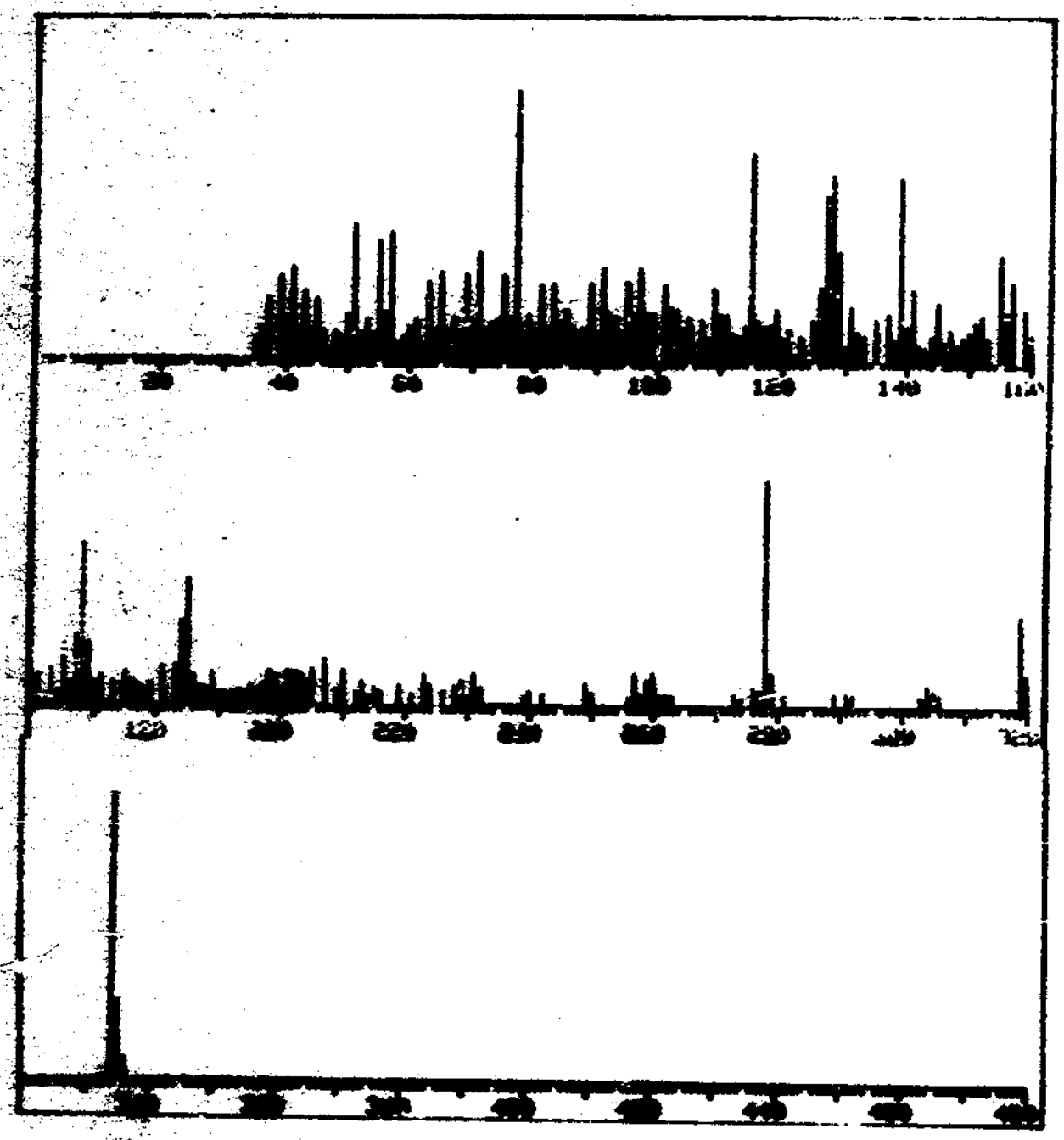


FIGURE 26: peak 19

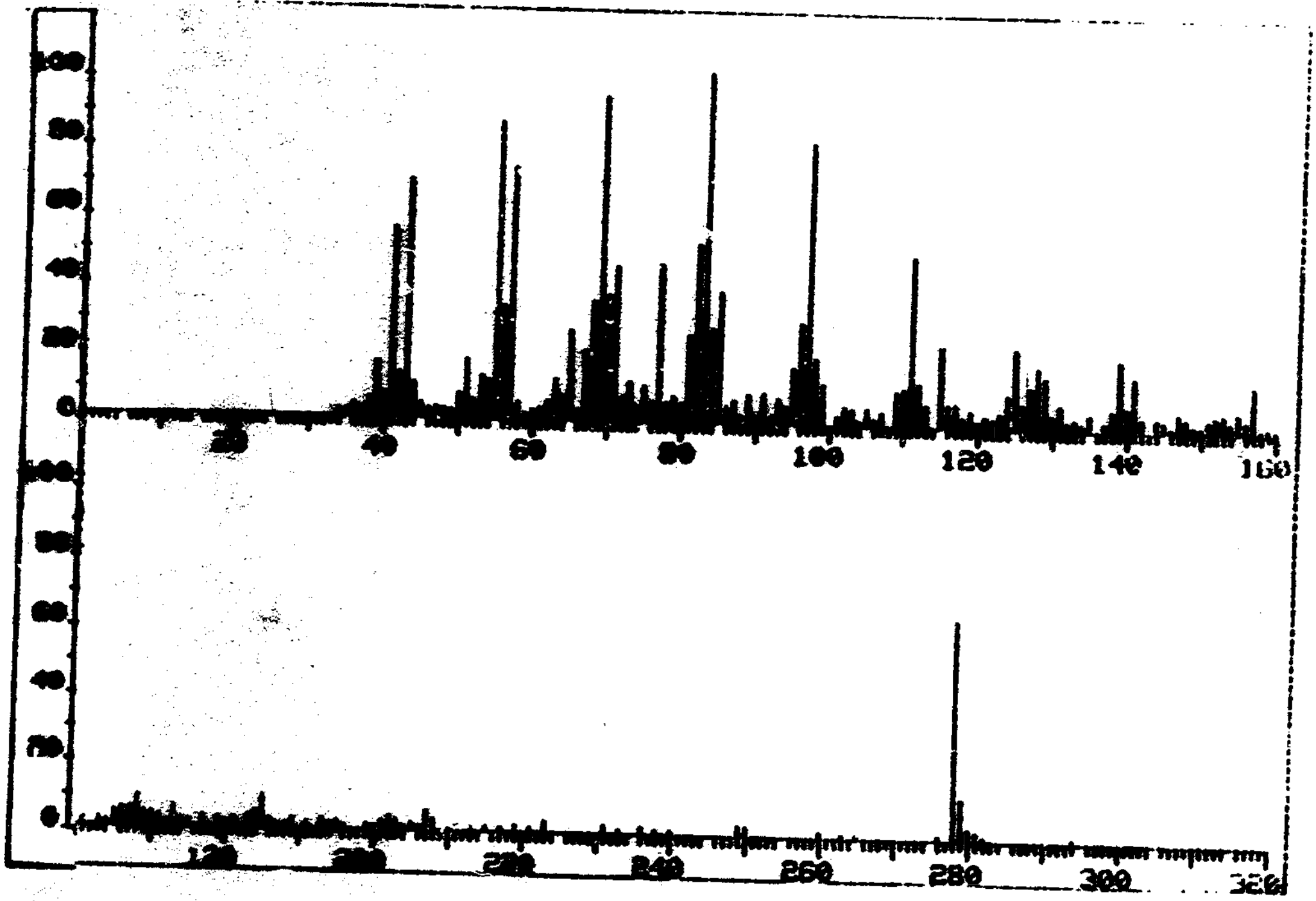


FIGURE 27: peak 20

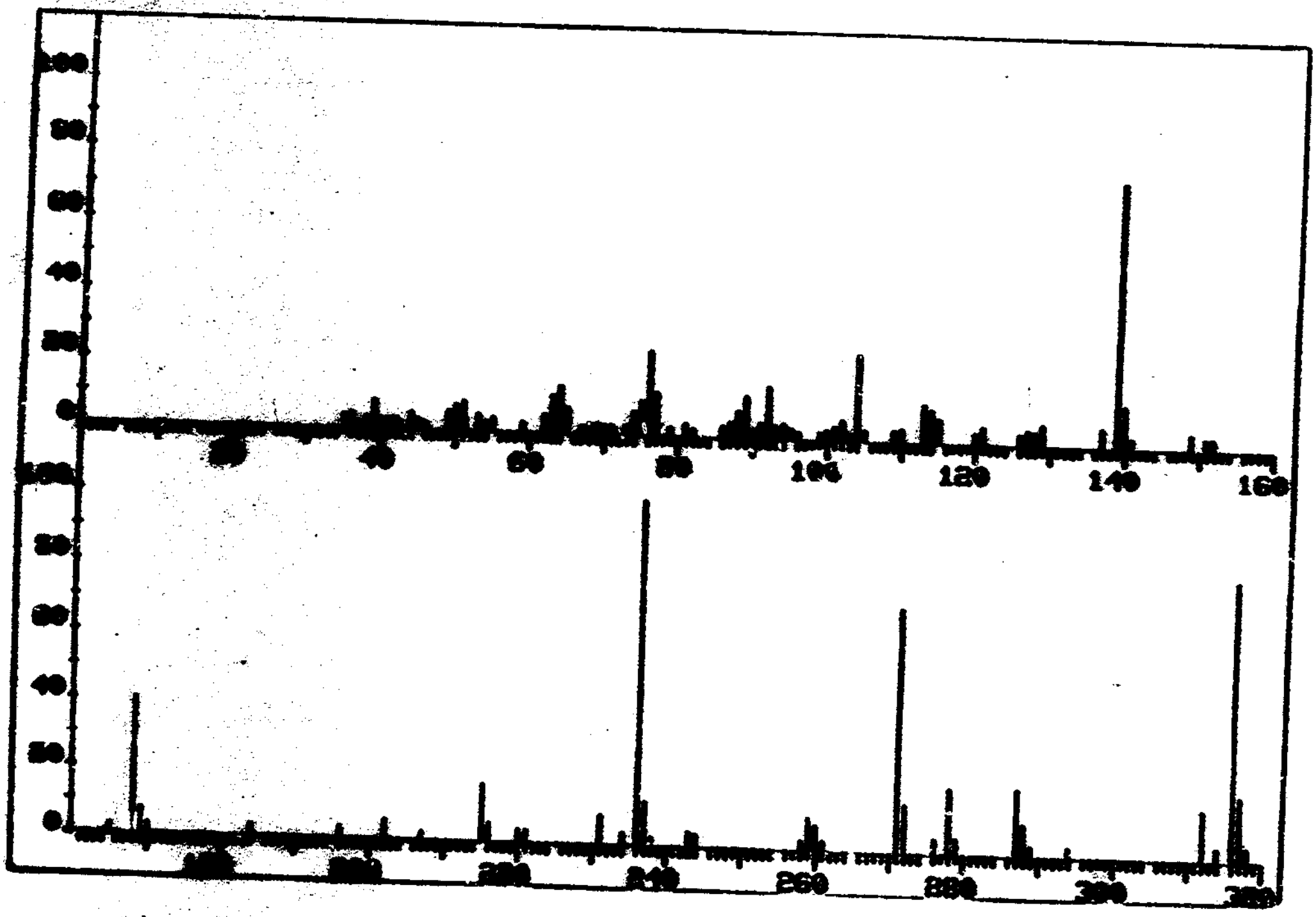


FIGURE 28: peak 21

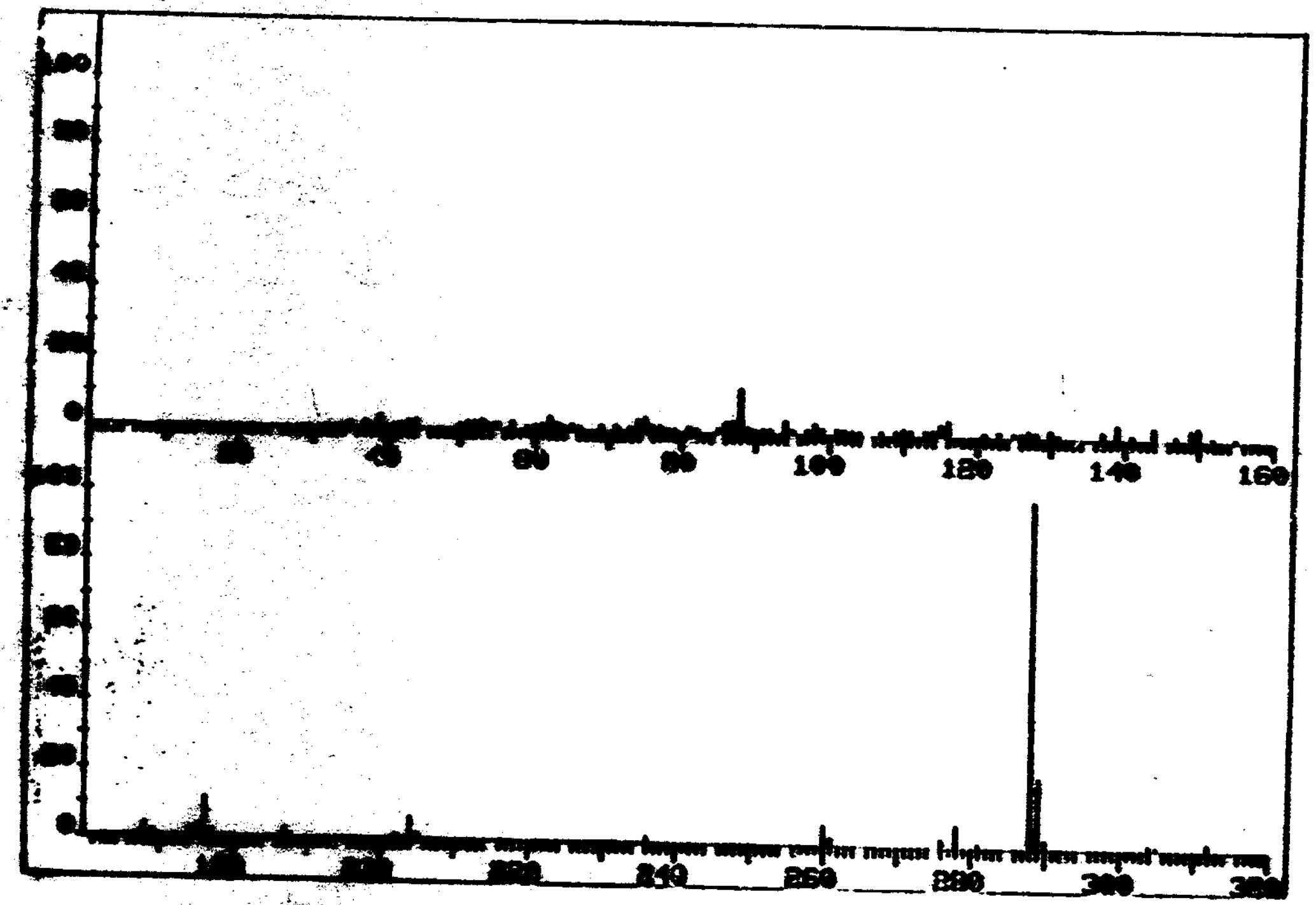


FIGURE 29: peak 22

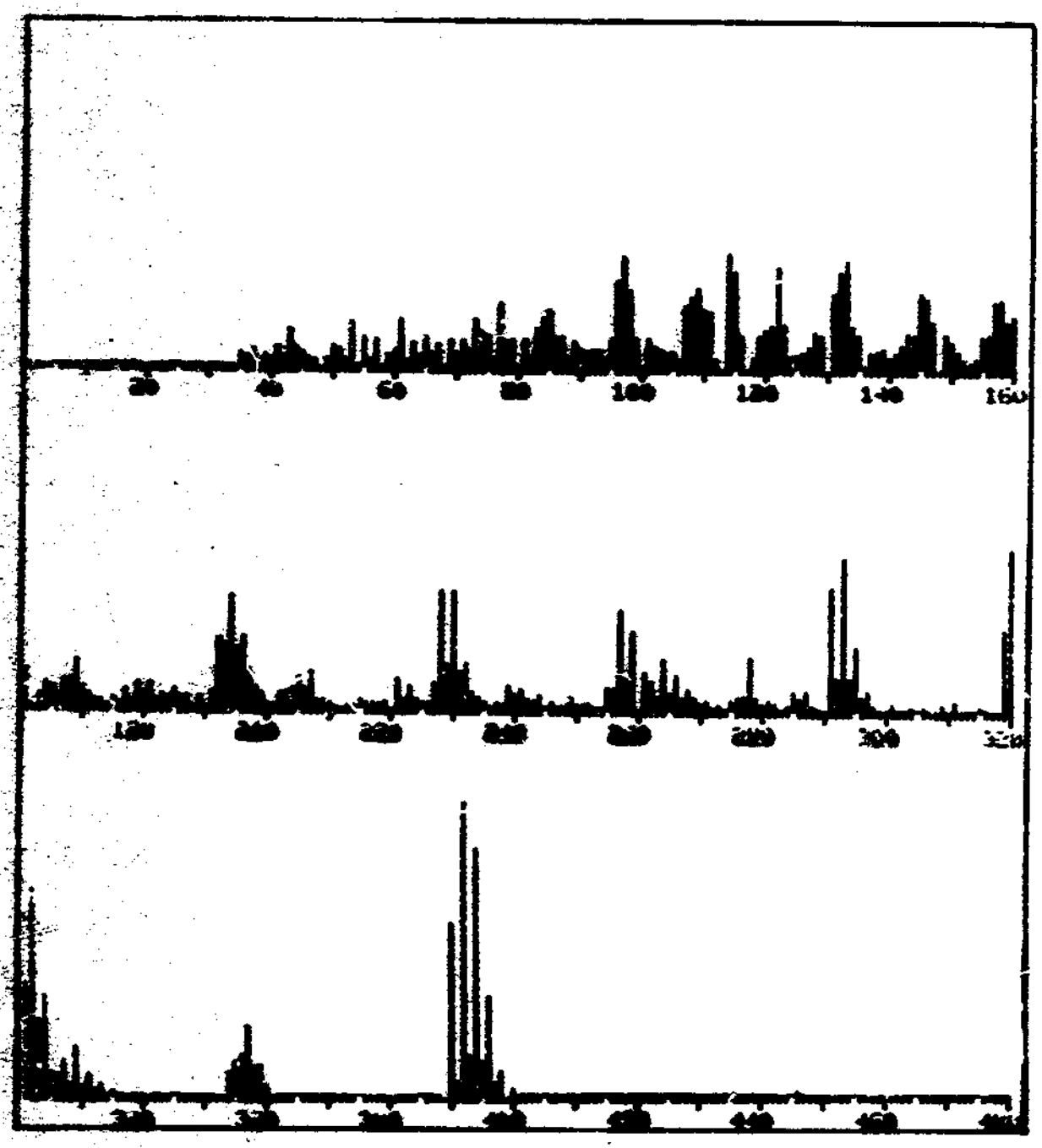


FIGURE 30: peak 23

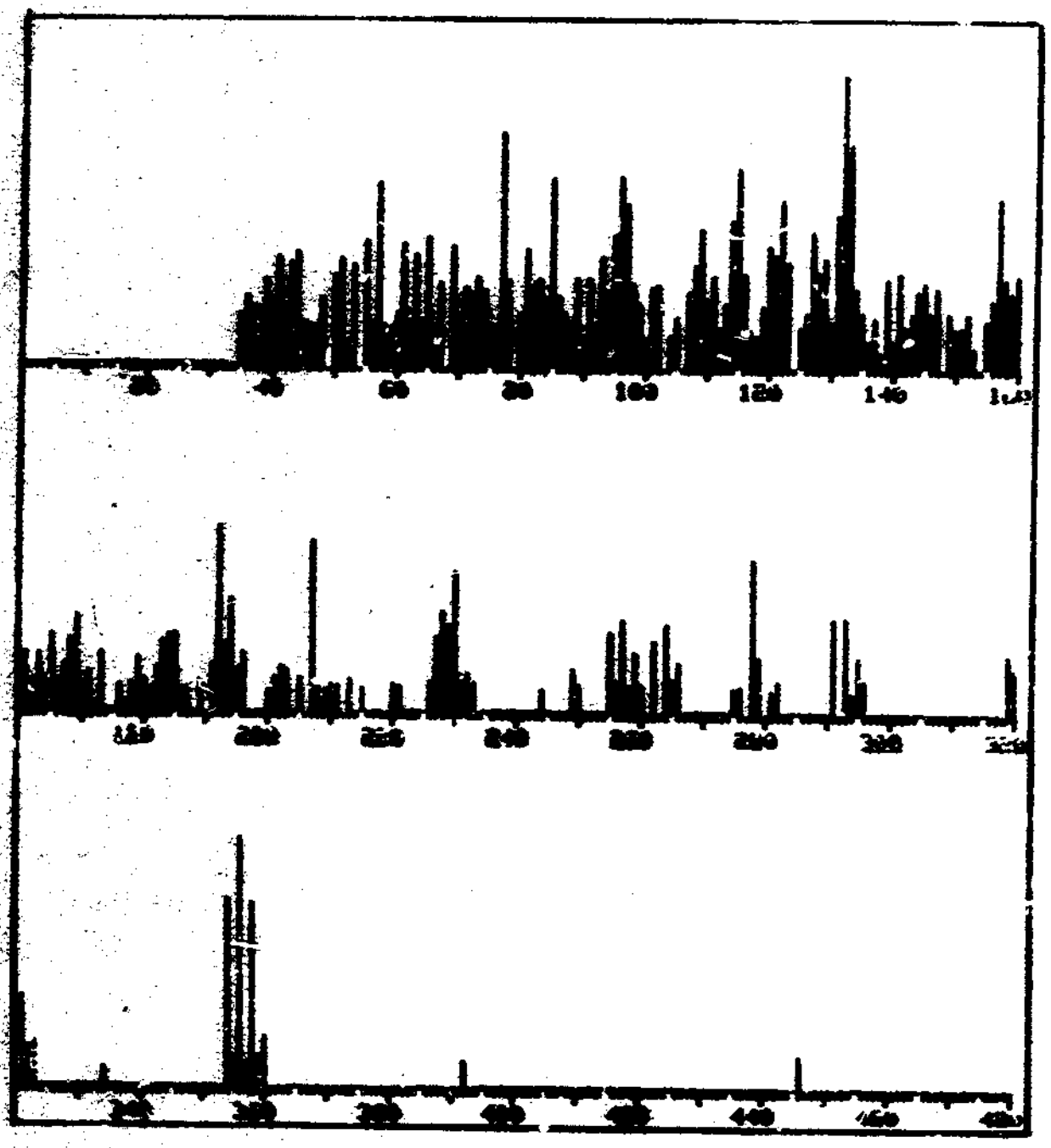


FIGURE 31: mark 24

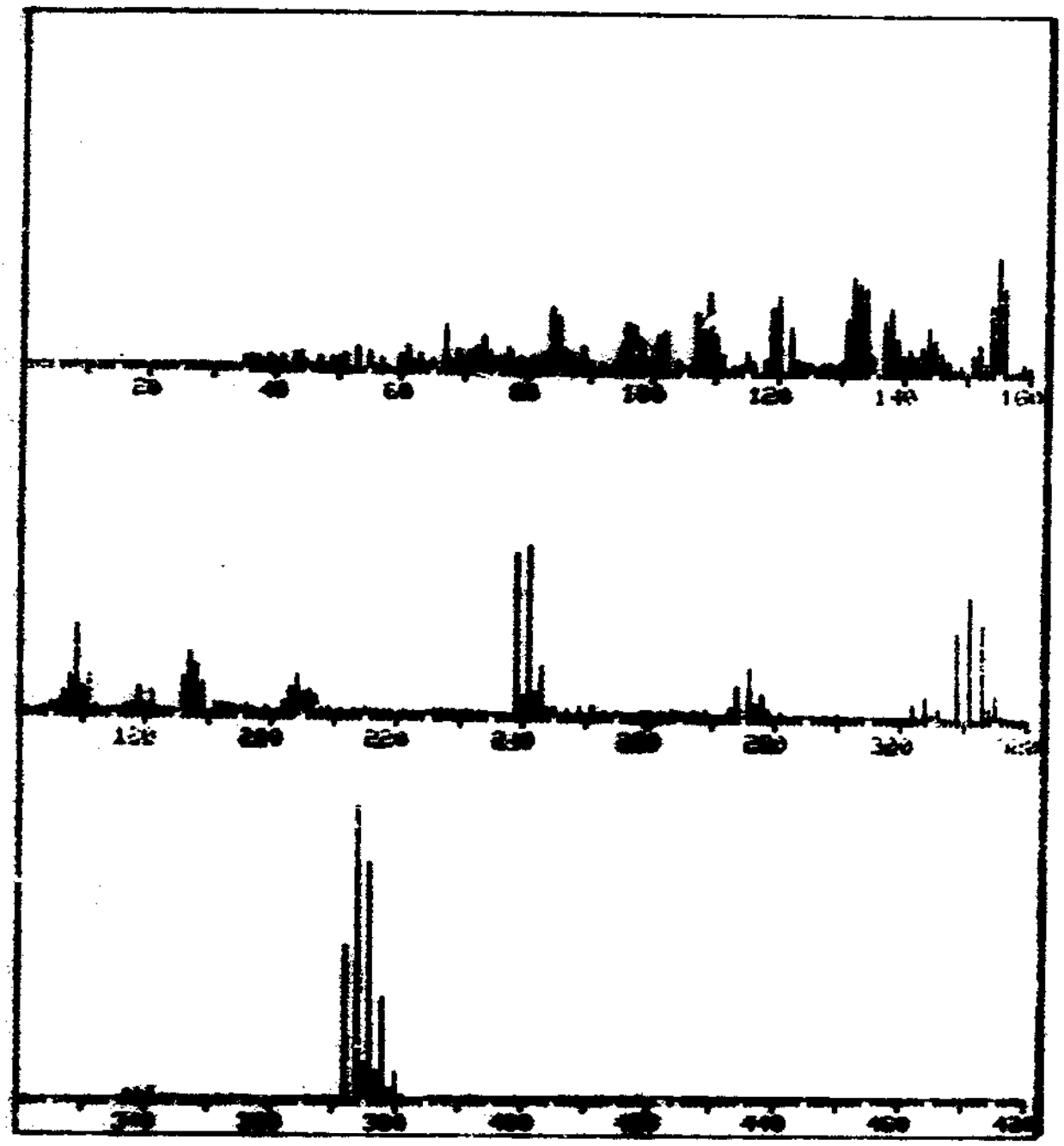
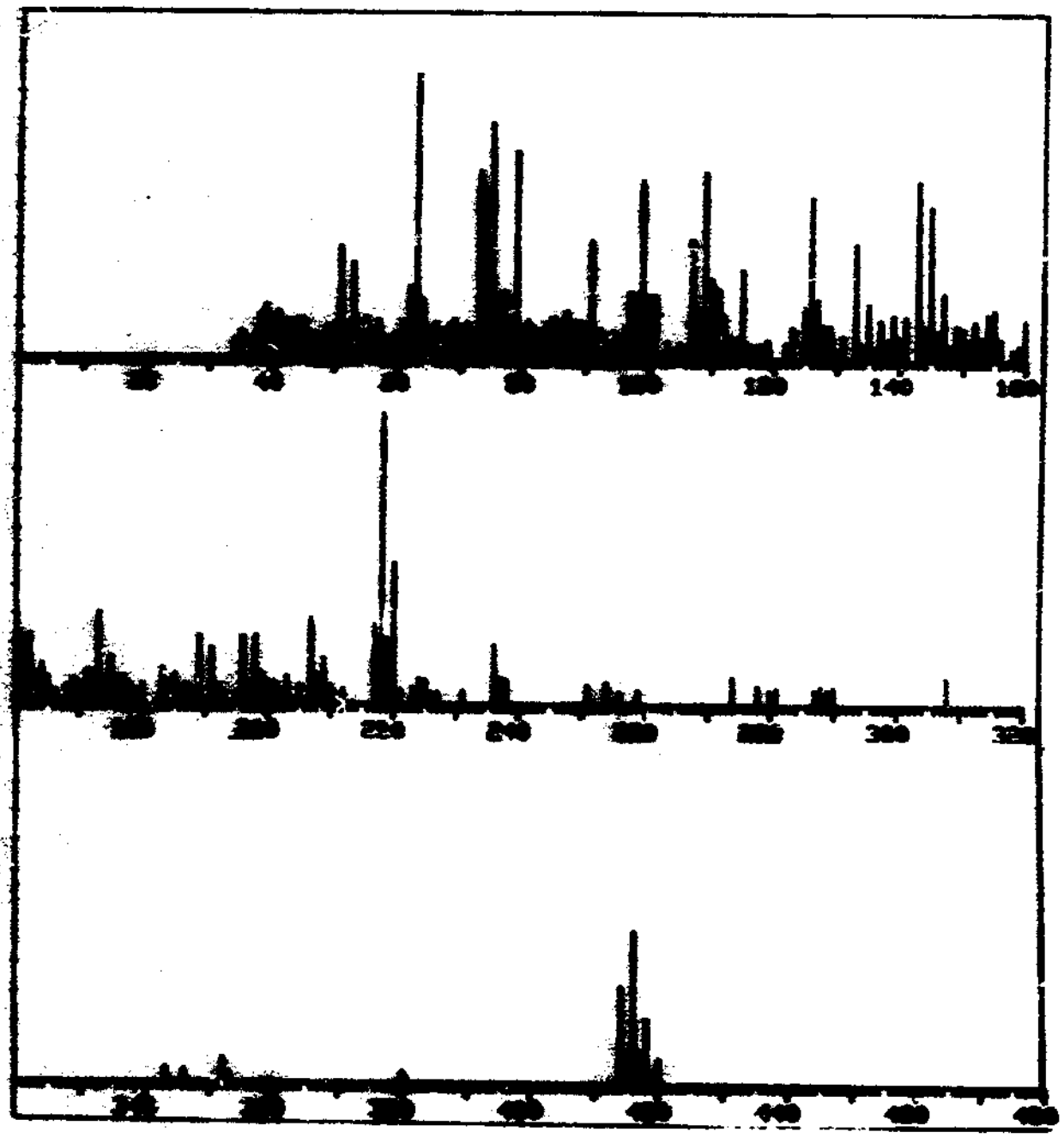


FIGURE 32: [illegible] 25



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FOOTNOTES

1. "Organic Reactions at Alumina Surfaces," an article by Gary H. Posner of Johns Hopkins University, was published in 1978 in Angewandte Chemie International Edition in English, 17, 487-496. The article is the most comprehensive review of alumina's catalytic properties in recent years.

There has been a great deal of research on aluminum oxide catalysis in the years following Posner's article. The following is an attempt to supplement the earlier article with the more recent information.

Due to the significance of the Posner article, the following owes a great deal to it. Many of the references are either taken directly from that article, or from Posner's subsequent work. Even the outline below comes largely from the article.

The following is in no way meant to substitute for the Posner article, but rather, to add to it. The reader is advised to study the earlier article for a more complete understanding of alumina catalysis.

2. Room temperature reaction conditions were used in all equations in this article unless otherwise noted.

3. No mechanism is provided, but the following seems likely.

4. Citation from Chen, A.S.C., Sneeyink, Fleesinger. Activated Alumina Adsorption of Dissolved Organic Compounds Before and After Ozonation. Department of Civil Engineering, University of Illinois-Urbana; Laboratoire Central, Lyonnaise des Eaux, La Jaca, France. Unpublished paper.

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6. Citation from E.A. Vaughan, Ph.D. thesis. University of Illinois-Urbana. 1964